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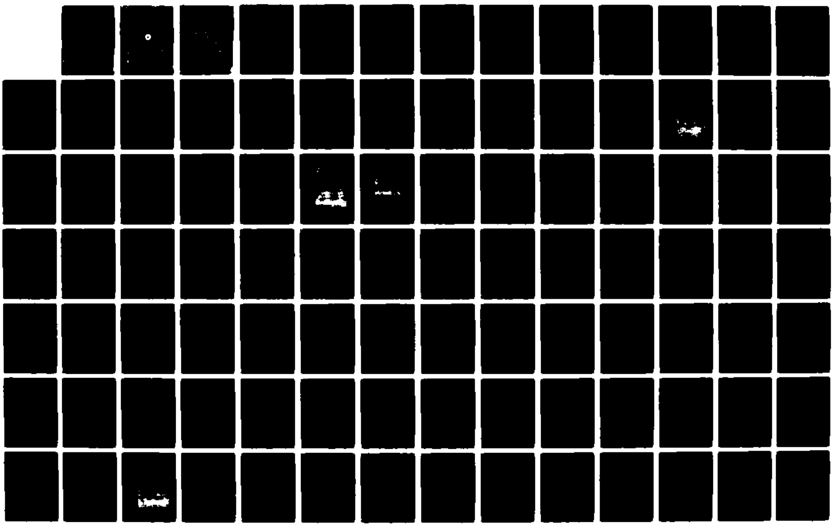

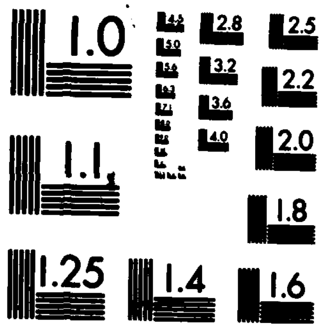

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16. Abstract

A laboratory scale experiment was conducted at the Coast Guard R&D Center during the winter 1979/1980 and winter 1980/1981 seasons to simulate the weathering of oil under Arctic conditions. The experiment consisted of weathering four types of oil (No. 2 heating oil, Prudhoe Bay crude oil, No. 4 fuel oil, and No. 6 fuel oil) in open boxes under environmental conditions for periods of up to a month. Samples were collected at various intervals for physical and chemical properties analysis.

The experiment focused on evaporation as the primary weathering process in the Arctic. Environmental conditions (temperature and wind speed) were monitored continuously to allow calculation of "evaporative exposure." Data analysis consisted of plotting the various physical and chemical parameters (density, viscosity, solubility, etc.), against "evaporative exposure", to study the quantitative dependence of the physical and chemical properties on evaporation.

The results indicate a well-defined functional dependence of several important physical properties on evaporation. This has led to a separate study by the University of Toronto to develop a simplified evaporation model. The results also identified two specific areas where further research is required; namely, the emulsification of oil and the combustion of oil under Arctic conditions.

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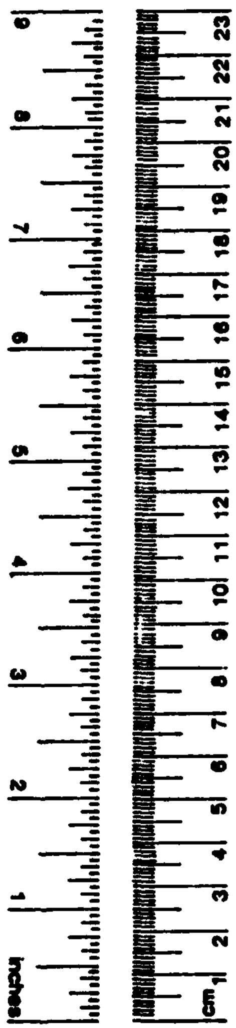
METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

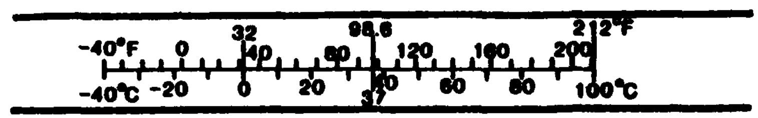
Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
		AREA		
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.8	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha
		MASS (WEIGHT)		
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
		VOLUME		
tsp	teaspoons	5	milliliters	ml
tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3
		TEMPERATURE (EXACT)		
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in ≡ 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures. Price $2.25. SD Catalog No. C13.10.286.



Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
		AREA		
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares (10,000 m^2)	2.5	acres	
		MASS (WEIGHT)		
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
		VOLUME		
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	0.125	cups	c
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	35	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3
		TEMPERATURE (EXACT)		
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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The authors would like to thank Dr. Don Mackay and his colleagues at the University of Toronto for their assistance in this endeavor. We also thank Dr. George Frame of the R&D Center Chemistry Branch for his assistance with the gas chromatography. Finally, special thanks goes to the personnel in Administrative Services for their assistance in the preparation of the manuscript.

SUMMARY

Oil weathering has been identified as the final phase in the evolution of an Arctic oil spill. It is a particularly important phase because it alters the physical and chemical properties of the oil which in turn affect the toxicity of the oil and the effectiveness of various containment and cleanup measures. It is therefore desirable to be able to predict the rate of weathering as a function of environmental conditions for various types of oil, and also predict the resulting physical and chemical changes in the oil.

Accordingly, a laboratory scale experiment was conducted at the Coast Guard R&D Center during the Winter 1979/1980 and Winter 1980/1981 seasons to simulate the weathering of oil under Arctic conditions. The experiment consisted of weathering four types of oil (No. 2 heating oil, Prudhoe Bay crude oil, No. 4 fuel oil, and No. 6 fuel oil) in open boxes under environmental conditions for periods of up to a month. Samples were collected at various intervals for physical and chemical properties analysis. The experiment focused on evaporation as the primary weathering process in the Arctic with other processes (dissolution, dispersion, and emulsification) being secondary in importance. Environmental conditions (temperature and wind speed) were monitored continuously to allow calculation of "evaporative exposure" using the formulation developed by Nadeau and Mackay (1978). Solar radiation was also monitored to study its effect on increasing the temperature of the oil.

Physical properties analysis for No. 2 heating oil, Prudhoe Bay crude, and No. 4 fuel oil included determination of density, viscosity, aqueous solubility, pour point, interfacial tension, flash point, fire point, and combustibility (ignition temperature, burn time, and burn efficiency). Only density values were obtained for No. 6 fuel oil as this oil showed no change with weathering. Chemical analysis consisted of running gas chromatograph (GC) scans of the samples, and computing GC hydrocarbon peak ratios referenced to the C_{20} peak height (i.e., C_{10}/C_{20}, C_{12}/C_{20}, C_{14}/C_{20}, C_{16}/C_{20} and C_{18}/C_{20}). Data analysis consisted of plotting the various physical and chemical parameters against "evaporative exposure", and studying the quantitative dependence of the physical and chemical properties on evaporation. Particular attention was given to the possibility of developing a simplified evaporation model.

The specific results of the data analysis can be summarized as follows:

(1) The density vs. evaporative exposure plots show a well-defined increase in density with weathering except where the oil samples were emulsified. Emulsification can increase oil density significantly independent of evaporative exposure levels. For oils where emulsification is not a factor, the increase in density can probably be modelled as a function of evaporative exposure.

(2) Oil/water interfacial tension decreases with weathering; however, there is no well-defined quantitative relation between interfacial tension and evaporative exposure.

(3) The aqueous solubility of all three oils decreased rapidly with weathering with a clear functional relationship between solubility and evaporative exposure.

(4) Viscosity increased significantly with weathering for Prudhoe Bay crude and No. 4 fuel oil. There was little change in the viscosity of the No. 2 heating oil. The results further show that the viscosity of the heavier oils is highly sensitive to emulsification, with emulsified samples attaining viscosity values of 10,000 centipoise independent of evaporative exposure levels.

(5) There is a well-defined increase in pour point as a function of evaporative exposure. In addition, the pour point appears to be relatively insensitive to emulsification.

(6) The plots of flash point and fire point show a clear dependence on evaporative exposure with both parameters increasing with exposure.

(7) The combustion tests were quantitatively inconclusive, and in conflict with the results of previous researchers. In a qualitative sense, the No. 2 heating oil was extremely difficult to ignite. On the other hand, various samples of Prudhoe Bay crude and No. 4 fuel oil which had been weathered for less than two weeks were ignited and burned with reasonable efficiency.

(8) Results of the solar radiation analysis indicates that heating of the oil by direct solar radiation under Arctic conditions will have little effect on the overall evaporation rates.

In a broader sense, the results of the experiment indicate that there is a well-defined quantitative relationship between the various physical properties and evaporative exposure levels, particularly where emulsification has not occurred. This supports the feasibility of developing an operational model to predict these properties based on evaporative exposure estimates. In addition, the results of the gas chromatograph analysis suggests that GC data (i.e., the C_{12}/C_{20} and C_{14}/C_{20} hydrocarbon peak ratios) may provide an index of weathering which can be used when evaporative exposure estimates are unavailable. Additional research should focus on correlating the physical properties and combustibility of weathered oils directly with the GC derived weathering parameters.

Finally, the study identifies two specific areas where our knowledge is lacking and additional research is required. The first is in our understanding of oil emulsification under Arctic conditions, both in the environmental mechanisms leading to emulsification, and in the resulting physical and chemical properties of the oil. The second is in the area of oil combustion, where little is known regarding the effects of the physical and chemical properties of the oil, and the external environmental conditions (i.e., temperature, wind speed, slick thickness, and underlying surface type) on oil ignitability and burning efficiency.

1.0 INTRODUCTION

The recent discovery of oil and gas along the Alaskan coast has led to full-scale exploration and development on shore. Offshore exploratory drilling has begun on the Continental Shelf and is certain to increase rapidly within the next several years. The best planning and most modern safety techniques cannot insure that accidental oil spills will not occur. Thus there is a definite need for oil spill models and cleanup contingency plans for Alaskan waters. Accordingly the Coast Guard Research and Development Center has been tasked with investigating the oil in ice problem in order to develop models for predicting the behavior and transport of oil spills in ice, and catalog the scientific information needed for planning effective cleanup operations.

As shown in Figure 1, the problem of predicting oil spill behavior in the Arctic is far more complex than for spills in temperate water, because of the changing ice conditions throughout the year. An oil spill in the Arctic will be subjected to a different sequence of physical and chemical processes depending on the time of year the spill occurs.

The evolution of a winter oil spill (Spill 1 in Figure 1) under a solid ice sheet has been described in detail by Lewis (1976). Such a spill will initially rise to the under surface of the ice where it will spread to some equilibrium thickness ranging from 1 centimeter to several tens of centimeters depending largely on the roughness and topography of the ice sheet. If the ice sheet is still growing, and if the oil remains stationary, the spill will eventually become entrapped within the ice until spring when warmer temperatures and increased solar radiation will cause the opening of brine drainage channels down through the ice sheet. Once these channels reach the entrapped oil, it will begin to migrate toward the surface. Eventually, the oil will reach the surface and collect in pools where it will be subject to various degradation processes collectively termed weathering. Likewise, if the oil is spilled on the surface of the water or ice (Spills 2, 3, 4, or 5), the oil will be immediately subject to various weathering processes.

Weathering will thus be the final phase in the evolution of an Arctic oil spill. It is a particularly important phase because it affects the physical and chemical properties of the oil which in turn determine the effectiveness of various cleanup measures. It also decreases the toxicity of the oil to animals and marine life due to the loss of the more volatile, more toxic fractions (Jordan and Payne, 1980). It is therefore desirable to be able to predict the rate of weathering as a function of environmental conditions for various types of oil, and also predict the resulting physical and chemical changes in the oil.

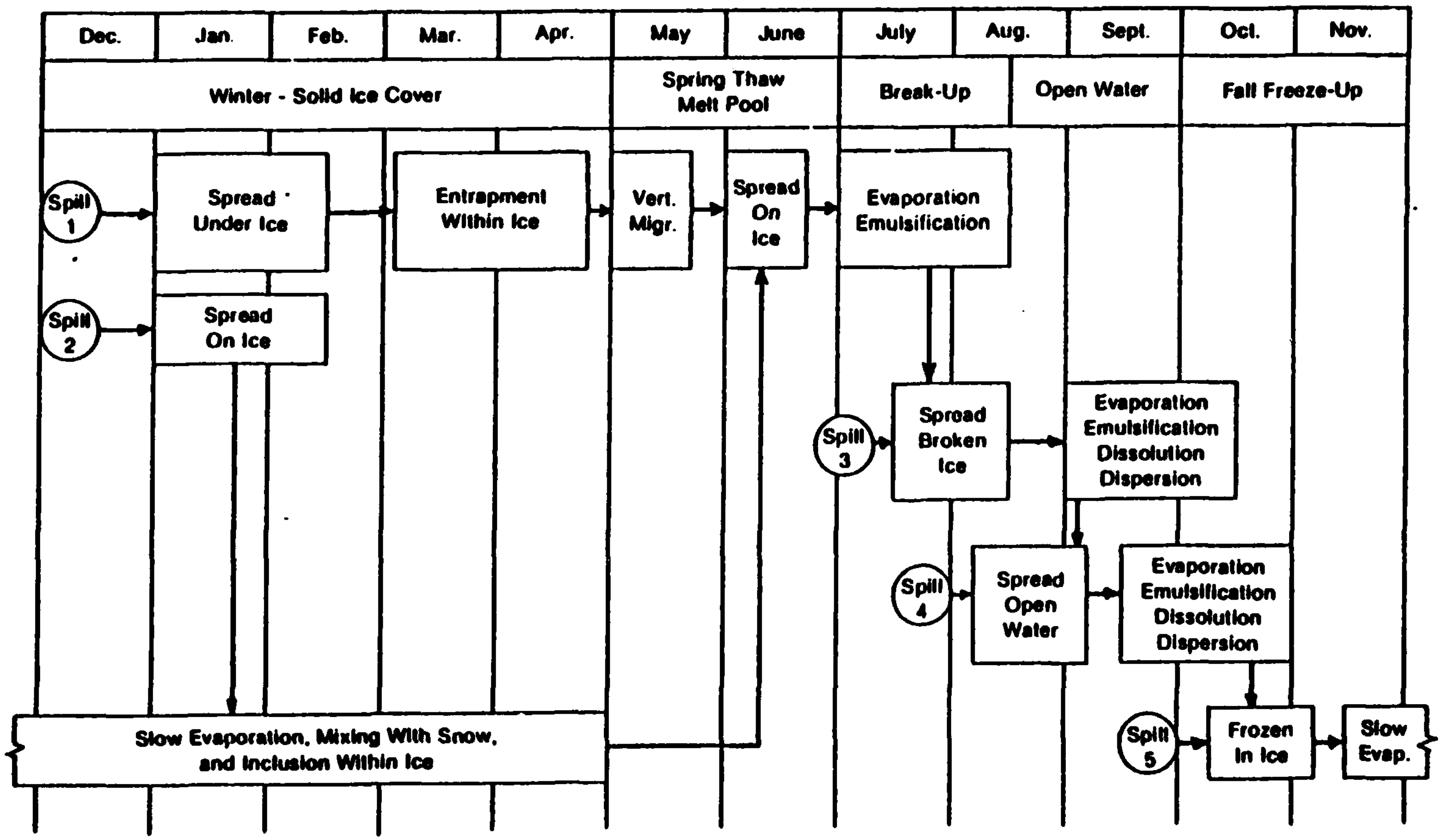

Figure 1 Schematic Showing Five Possible Evolutions of an Arctic Oil Spill.

2.0 BACKGROUND ON OIL WEATHERING UNDER ARCTIC CONDITIONS

2.1 Weathering Processes

In temperate waters, the term weathering encompasses a number of physical, chemical, and biological processes including evaporation, dissolution, dispersion, emulsification, chemical oxidation, polymerization, and microbial degradation. Under Arctic conditions, the last three processes can be neglected as they are extremely slow or non-existent.

Immediately after the oil is exposed to the atmosphere, evaporation becomes the predominant weathering process. If the oil is spilled on a solid ice surface, then evaporation is the only significant weathering process. Evaporation results in the rapid loss of the lighter components of the oil to the atmosphere, decreasing the spill volume and altering the physical and chemical properties. The evaporation rate decreases with time as the lighter components are depleted, and only the heavier, less volatile components remain.

If the oil spreads on the surface of melt ponds, or enters open water areas, then the lighter fractions of the oil will begin to dissolve into the water column. For the open water case, wind-generated turbulence may physically disperse the oil into the water column as well. Mackay and Leinonen (1977) have shown that both processes are significant in increasing the hydrocarbon concentration in the water column, and that for any appreciable turbulence, dispersion will predominate by two orders of magnitude in removing hydrocarbons from the spill. They have also predicted that although evaporation will be the predominant process immediately after the spill, within a few days the amount of oil dissolved and dispersed will be comparable to that evaporated. Therefore, dissolution and dispersion can significantly decrease the volume of oil remaining in an open water spill. Dissolution of the lighter ends will also alter the physical properties and toxicity of the oil remaining in the slick.

In addition, wind-generated mixing in melt ponds or in open water may cause the formation of highly stable water-in-oil emulsions. Emulsification may in turn drastically alter the physical properties of the oil, particularly the density, viscosity, and combustibility. Emulsification does not directly remove oil from the spill, and may in fact stabilize the oil volume in the spill, decreasing the rates of oil loss due to evaporation, dissolution, and dispersion.

2.2 Field Observations

Researchers have investigated the mechanisms and effects of oil weathering under field conditions during experimental and accidental oil spills. Particular attention has been paid to evaporation as the predominant weathering process. Glaeser and Vance (1971) conducted experimental spills in a melt pond under summer Arctic conditions with Prudhoe Bay crude, allowing the oil to weather for 13 days. They observed significant slick weathering with the oil becoming thick and gummy by the end of the period. Physical properties analysis showed that the oil density changed linearly with time (0.89-0.96 g/cm^3), and that the viscosity increased significantly (300 cp to $>$1000 cp at 0^oC). Air oil interfacial tension values changed slightly (28-31 dynes/cm). Boiling point distillation curves for the samples indicated that all of the volatiles were lost within 5 days.

McMinn and Golden (1973) conducted similar experiments with Prudhoe Bay crude under winter Arctic conditions. They studied two 50-gallon spills, one on smooth ice and one in snow, over a 15-day period. They noted that although weathering is slower than in the summer, oil does in fact weather during the winter. They also noted that weathering is decreased by snow cover which isolates the oil from the air, particularly during periods of high winds.

NORCOR (1975) studied the weathering of two northern crudes (Norman Wells crude and Swan Hills crude), both in ice and on the surface of the ice, for periods up to a month. They found that when the oil was trapped within the ice, weathering was negligible. However, once on the surface, the lighter ends evaporated rapidly, with 18-19% volume loss for Swan Hills and 28-37% loss for Norman Wells crude. Physical properties analysis showed an increase in density, viscosity, and pour point, and a decrease in solubility for both oils.

Deslauriers et al. (1977) investigated the weathering of No. 2 home heating oil during the Buzzards Bay spill. Oil samples collected after 12 days of weathering indicated evaporation losses of 6%-47% depending primarily on the location of the oil in the ice. For instance, oil sheltered by an overlying rafted ice sheet showed only 6% loss, while oil on exposed ice surfaces showed 28-47% loss.

Field observations for other weathering processes, dissolution, dispersion, and emulsification, are limited. Water column sampling by NORCOR (1975) in the area of an under ice crude oil lens showed hydrocarbon levels typically ranging from 10-20 ppm. Likewise, water column and sediment sampling by Deslauriers et al. (1977) during the Buzzards Bay spill indicated that hydrocarbon levels throughout the spill site were much less than those that would be expected under comparable open water conditions. This indicates that dissolution and dispersion are secondary to evaporation in depleting the spill. This seems reasonable because of the absence of turbulent mixing to disperse the oil in ice-covered waters. Field data on emulsification under Arctic conditions, except for a few qualitative observations, are essentially non-existent.

2.3 Modelling of Weathering Processes

A number of attempts have been made by various researchers to mathematically model the weathering processes discussed above. In particular, Leinonen and Mackay (1975), Mackay and Leinonen (1977), Nadeau and Mackay (1978), and Mackay et al. (1980) have documented the development of theoretical and empirical models to predict the rate of weathering, and its effect on the physical and chemical properties of both crude oils and refined oil products. Mackay and Leinonen (1977) developed a comprehensive oil spill model which encompassed all four weathering processes. Mass transfer equations were developed for each process to predict the amount of oil lost from a spill due to evaporation, dissolution, emulsification and dispersion. The model also predicts the physical properties and chemical composition of the oil, and the hydrocarbon concentration in the water column.

More recently, Nadeau and Mackay (1978) have developed a simplified model which focuses on evaporation as the predominant weathering process, and ignores dissolution, dispersion, and emulsification as being secondary in importance, at least in the early stages of the spill. They developed a semi-empirical formulation for determining the amount of oil evaporated as a function of wind speed, spill area, temperature, type of oil, and exposure time. In their investigations, they were able to produce a series of evaporation curves for various petroleum products, an example of which is shown in Figure 2. In this graph, the mass fraction of the petroleum product remaining is given as a function of temperature and the "evaporative exposure", KAt. This parameter, KAt, is the product of the mass transfer coefficient, K, the area factor, A, and the exposure time, t, where:

K(m/sec) is a function of the wind speed (e.g., $K=0.0025\ W^{0.78}$)

$$A(m^2/kg) \text{ is } \frac{(\text{spill area})}{(\text{spill volume})(\text{oil density})}$$

and t is the exposure time in secs.

The temperature indicated in the graph is the temperature at the oil/air interface. This temperature is in turn affected by the temperature of the underlying surface (i.e., water or ice), the oil temperature, and the air temperature. The temperature of the oil may be greater than either the air temperature or underlying surface temperature if the oil is subjected to intense solar radiation. In their discussion of this simplified model, Nadeau and Mackay (1978) have outlined a step-by-step procedure for calculating the extent of evaporation for a specific type of oil spilled, a given exposure time, and a given set of environmental conditions.

In extending the simplified approach, Mackay et al. (1979) and Mackay and Paterson (1980) have developed an empirical model for estimating the various physical property changes of a specific type of oil as a function of evaporative exposure. Typical results for this type of model are shown in Figure 3. Using the graph, the predicted physical properties of a spilled oil could be easily determined, and this information incorporated into a cleanup strategy.

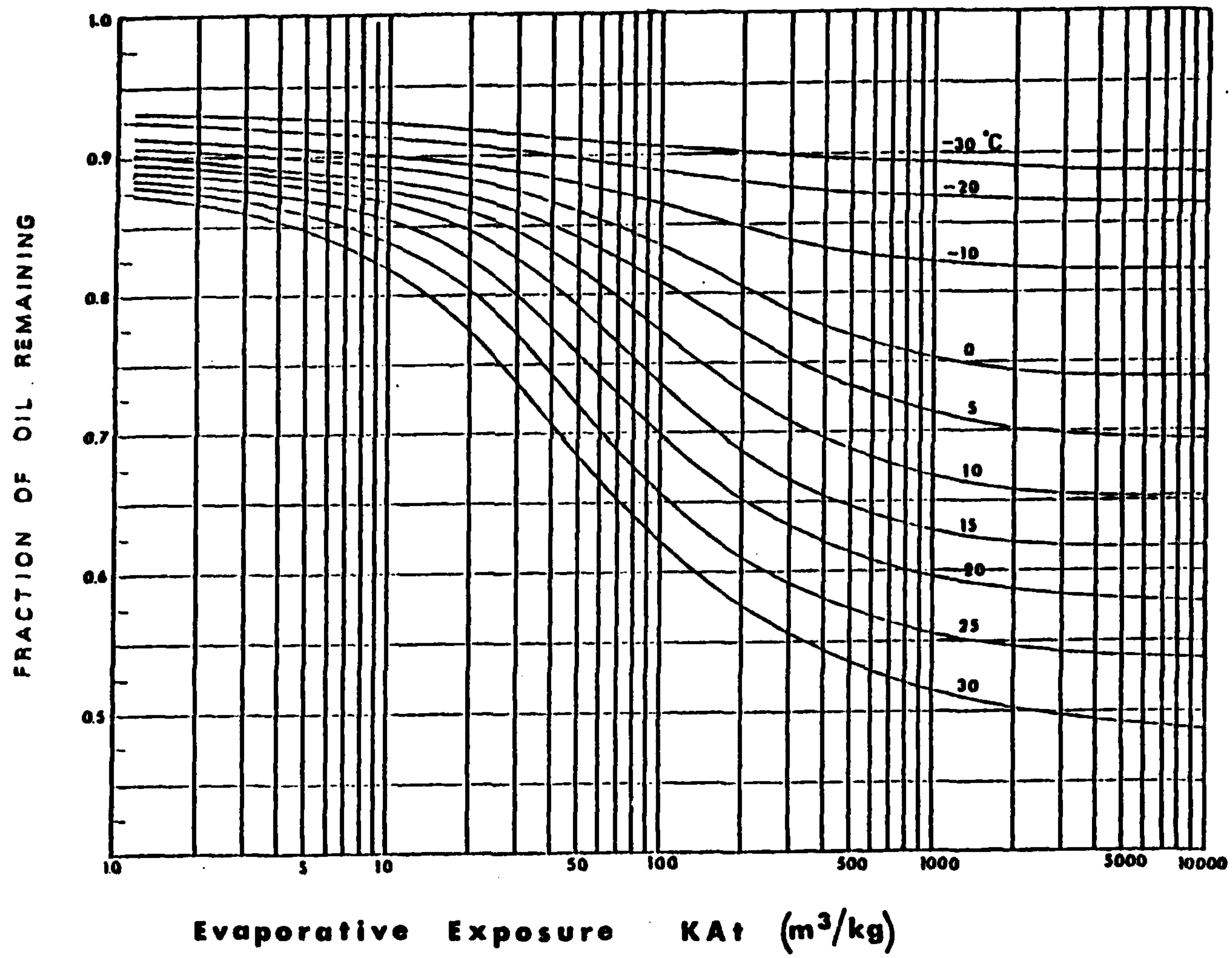

FIGURE 2. EVAPORATION CURVES FOR LIGHT AND MEDIUM CRUDE OILS (FROM NADEAU AND MACKAY, 1978)

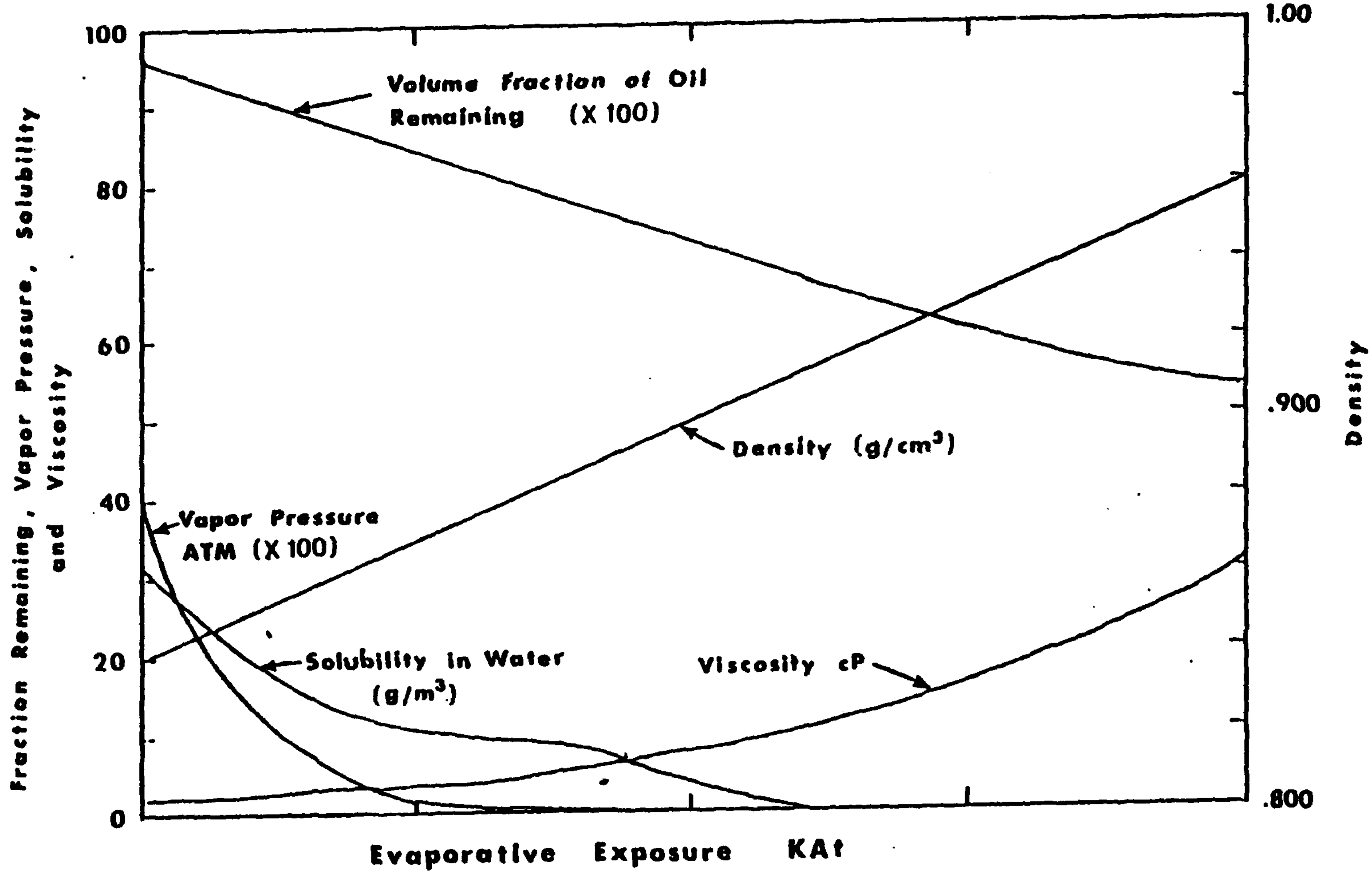

FIGURE 3. OIL PROPERTIES AS A FUNCTION OF EVAPORATIVE EXPOSURE

3.0 OBJECTIVES OF THE WEATHERING EXPERIMENT

The degree of weathering, and the resulting physical and chemical changes of the oil, is of primary importance in determining the effectiveness of various oil spill countermeasures. Furthermore, previous research indicates that evaporation is the primary weathering process under Arctic conditions, allowing the other weathering processes to be ignored. This simplification, together with the existence of a simplified evaporation model as developed by Nadeau and Mackay (1978), suggested that additional research in this area might provide the Coast Guard with an important modelling capability, with a minimum of research effort.

Accordingly, a laboratory scale experiment was conducted at the Coast Guard R&D Center during the Winter 1979/80 and Winter 1980/81 seasons to simulate the weathering of oil under Arctic conditions. The experiment consisted of weathering various types of oil in open boxes under environmental conditions for periods of up to a month. Samples were collected at various intervals for physical and chemical analysis. The experiment focused on evaporation as the primary weathering process with environmental conditions (temperature and wind speed) monitored continuously to allow calculation of hourly "evaporative exposure" values. Solar radiation was also monitored to study its effect on increasing the temperature of the oil.

The first objective of the experiment was to document the effect of evaporation on oil weathering under Arctic conditions, and its role in determining the mass fraction remaining, and the physical and chemical properties of the oil. Of particular interest with regard to the physical properties was the density, viscosity, and combustibility of the oil, as these properties are likely to dictate the effectiveness of various cleanup measures (i.e., skimming, use of suction hoses, burning, etc.).

The second objective was to verify the dependence of the rate of evaporation (i.e., mass remaining) on the evaporative exposure (temperature, wind speed, and time), and then verify the accuracy of the empirical formulations of Nadeau and Mackay (1978) in modelling this dependence. Likewise, particular interest was given to verifying and possibly refining the empirical models for predicting physical properties as a function of evaporative exposure. This second objective has subsequently led to a cooperative effort with Dr. Mackay at the University of Toronto in producing a comprehensive evaporation model. This model will be covered in a separate University of Toronto report (Mackay et al., 1982).

The third objective of the experiment was to investigate the dependence of the oil/air interface temperature on the air temperature, underlying surface temperature, and solar radiation. Of particular interest was the role of solar radiation in raising the temperature of darker oils above ambient environmental levels.

4.0 EXPERIMENTAL APPARATUS AND PROCEDURES

The oil weathering experiments were carried out on the roof of the main R&D Center building at Avery Point, Groton, Connecticut (Figure 4a). This location offered a marine environment with ample exposure to the elements. It was hoped that during the winter months, this environment would approximate conditions on the North Slope of Alaska during late spring and summer, when large quantities of oil would most likely reach the surface of the ice.

The experimental apparatus consisted of plywood weathering boxes (60 cm x 60 cm x 30 cm deep) as shown in Figure 4b. Each box was lined with 5 cm of styrofoam insulation and fitted with a polyethylene liner to make the boxes reusable. Transparent covers were also fabricated so that the weathering oil samples could be protected from rain and snow as desired.

The experimental procedure called for freezing a block of fresh water ice in each box in the R&D Center cold room. The boxes were then transported to the roof where a 400 ml sample of either No. 2 home heating oil, No. 4 fuel oil, No. 6 fuel oil, or Prudhoe Bay crude was deposited on the ice surface. The No. 2, No. 4, and No. 6 oils were obtained from local University of Connecticut physical plant stocks at Avery Point. The Prudhoe Bay crude oil was obtained courtesy of the Atlantic Richfield Company. In warmer weather, the oil was initially deposited in a (30 cm x 30 cm) cavity chipped in the center of the ice block to prevent the oil from running down the sides of the block. Usually after a few days enough melt water was present so that the oil covered most of the surface area inside the box. The oil samples were then allowed to weather for periods ranging from approximately 1 day to 1 month. At specified times during the period, a sample of each type of oil would be removed from the weathering boxes. These samples would be analyzed to determine mass fraction remaining, and the physical and chemical properties of the oil.

Temperatures, wind speed, and solar radiation were monitored continuously. Wind speed and ambient air temperature on the roof were monitored using an MRI mechanical weather station. Air temperature, oil surface temperature, and ice/water temperature were monitored using YSI (Yellow Springs Instrument Co.) Series 400 thermistors tied into an Instrulab 2000 datalogger. Solar radiation values were monitored using an Eppley PSP pyranometer with a Hollis MR-5 pyranometer as backup. Complete specifications for all environmental monitoring instrumentation are given in Appendix A.

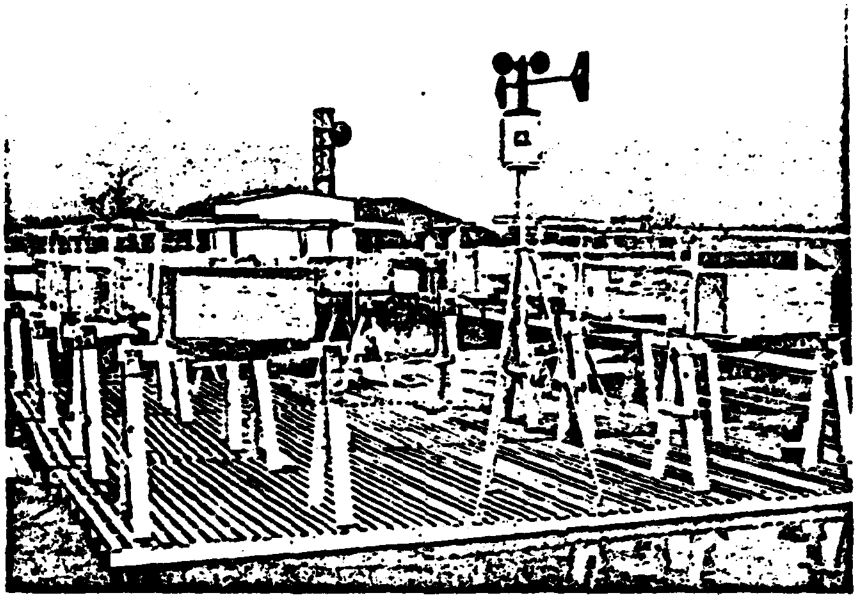

Figure 4a. Photograph showing oil weathering experiment test site on the roof of the R&D Center

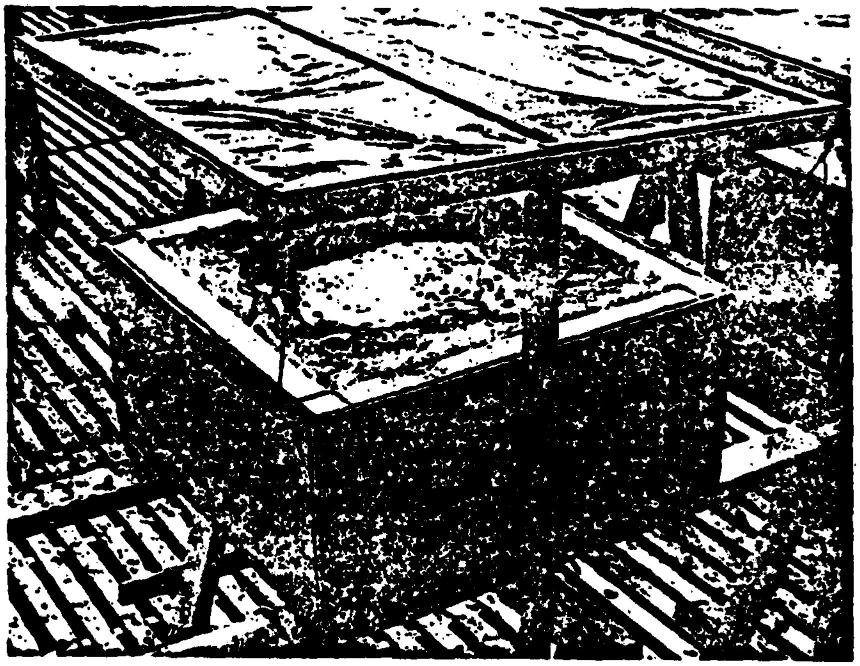

Figure 4b. Photograph showing the oil weathering box with oil sample and rain screen in place

5.0 ENVIRONMENTAL DATA AND SAMPLE ANALYSIS

Data analysis for the experiment involved computing the evaporative exposure values, KAt (Nadeau and Mackay, 1978), for each of the samples recovered, and analyzing each sample for mass fraction remaining, and physical and chemical oil properties. The evaporation rate and physical and chemical parameters for each oil were then plotted as a function of evaporative exposure.

Environmental data analysis was conducted at the R&D Center and involved computing hourly values of evaporative exposure and then summing these values for the weathering period of each sample to obtain a cumulative evaporative exposure for each sample. The hourly values of temperature and solar radiation were also analyzed for specific weathering periods to study the dependence of the oil temperatures on air temperature and underlying surface temperature, and on the levels of direct solar insolation.

The physical and chemical analysis of the oil samples was accomplished jointly by the R&D Center and the University of Toronto. All samples were analyzed at the R&D Center for mass fraction remaining and various physical properties including specific gravity (at 25°C), viscosity (at 20°C), water content, flash point, fire point, and combustibility (ignition temperature, burning time, and burning efficiency). Chemical analysis at the R&D Center involved running gas chromatograph scans on each sample to delineate its chemical composition. The analysis methods used at the R&D Center are outlined in detail in Appendix B. Based on the initial results of the R&D Center analysis, various samples of the No. 2 oil, No. 4 oil, and Prudhoe Bay crude oil were selected for further analysis by the University of Toronto. Physical properties analysis by the University of Toronto included determination of density (at 0°C and 20°C), interfacial tension (at 20°C), aqueous solubility (at 20°C), viscosity (at 0°C, 10°C, 20°C, and 30°C), pour point, flash point and fire point. Chemical analysis by the University of Toronto included gas chromatograph analysis and boiling point distillation analysis for selected samples. In addition, a laboratory air bubbling evaporation experiment was conducted on unweathered samples of the oil to further define the dependence of mass fraction remaining, and the physical and chemical properties of the oil, on the degree of evaporation. The analyses performed at the University of Toronto, together with the results, are described in detail in the University of Toronto report by Mackay et al., 1982.

6.0 RESULTS OF THE OIL WEATHERING EXPERIMENT

6.1 General Observations

Altogether, 109 weathered oil samples (30 No. 2 oil, 31 No. 4 oil, 35 Prudhoe Bay crude, and 13 No. 6 oil) were collected and analyzed for the Winter 1979/80 and Winter 1980/81 experiments. In addition, unweathered standard samples of each type of oil were taken at intervals throughout the experiment period, to establish baseline physical and chemical properties for each type of oil. The time weathering began, time weathering ended, duration of weathering in hours, average temperature during the weathering period, average wind speed during the weathering period, and cumulative evaporative exposure for each weathered sample are given in Tables 1a-1d. The time of year during which the samples were weathered, the condition of the underlying surface, and the prevailing weather conditions during certain weathering periods have led to specific groupings of the samples for the various types of oil as outlined below.

Group	Weathering Period	Samples
	No. 2 Home Heating Oil	
Winter 1980	11 Feb-25 Feb 1980	1-7
Winter 1981	6 Jan-25 Feb 1981	8-18
Spring 1981	10 Mar-26 Mar 1981	19-30
	Prudhoe Bay Crude	
Winter 1980	4 Feb-22 Feb 1980	1-8
Winter 1981	1 Dec-4 Feb 1980	9-18
Winter 1981	3 Feb-26 Feb 1981	19-25
(emulsified)	10 Mar-13 Apr 1981	34-35
Spring 1981	2 Mar-30 Mar 1981	26-33
	No. 4 Fuel Oil	
Winter 1980	18 Feb-6 Mar 1980	1-6
Winter 1981	6 Jan-4 Feb 1981	7-14
Winter 1981	3 Feb-26 Feb 1981	15-21
(emulsified)	2 Mar-6 Apr 1981	25,27,29,30
Spring 1981	2 Mar-13 Apr 1981	22-24,26,28,31

Table 1a Environmental Data For No.2 Heating Oil.

#	SAMPLE	START TIME/DATE	END TIME/DATE	HOURS	AVERAGE TEMP DEG C	AVERAGE WIND M/SEC	EVAP EXPOSURE X 10^{-6}
01	No2 #01	1000 11 FEB 80	0900 12 FEB 80	023	-.2	4.2	.559
02	No2 #02	1000 11 FEB 80	1000 13 FEB 80	048	-.8	3.5	1.021
03	No2 #03	1000 11 FEB 80	1000 15 FEB 80	101	-3.2	3.5	2.105
04	No2 #04	1000 11 FEB 80	1400 18 FEB 80	172	-1.4	3.5	3.582
05	No2 #05	1000 11 FEB 80	0900 25 FEB 80	335	.7	3.0	6.219
06	No2 #06	1000 11 FEB 80	SAMPLE LOST	000	—	—	0.000
07	No2 #07	1200 20 FEB 80	1400 21 FEB 80	026	4.1	1.5	.278
08	No2 #08	1400 06 JAN 81	1300 07 JAN 81	023	.4	4.0	.547
09	No2 #09	1400 06 JAN 81	0800 10 JAN 81	090	-5.9	3.0	1.645
10	No2 #10	1400 06 JAN 81	0900 12 JAN 81	139	-8.1	3.2	2.730
11	No2 #11	1400 06 JAN 81	0900 15 JAN 81	211	-8.6	2.8	3.693
12	No2 #12	1400 06 JAN 81	1000 19 JAN 81	308	-7.5	2.8	5.450
13	No2 #13	1400 06 JAN 81	0900 22 JAN 81	379	-6.4	2.6	6.325
14	No2 #14	1400 06 JAN 81	0900 29 JAN 81	547	-4.3	2.6	9.090
15	No2 #15	1400 06 JAN 81	0900 04 FEB 81	691	-4.0	2.8	12.072
16	No2 #16	0900 03 FEB 81	0900 05 FEB 81	048	-8.2	3.0	.896
17	No2 #17	0900 03 FEB 81	0900 09 FEB 81	144	-3.7	2.9	2.631
18	No2 #18	0800 25 FEB 81	1600 25 FEB 81	008	5.0	4.2	.200
19	No2 #19	1100 10 MAR 81	0900 11 MAR 81	022	2.9	2.1	.305
20	No2 #20	1100 10 MAR 81	0900 12 MAR 81	046	2.4	2.7	.787
21	No2 #21	1100 10 MAR 81	1100 14 MAR 81	096	3.2	4.1	2.250
22	No2 #22	1100 10 MAR 81	1100 16 MAR 81	144	2.6	4.4	3.633
23	No2 #23	1100 10 MAR 81	1200 18 MAR 81	193	1.5	4.5	4.951
24	No2 #24	1100 10 MAR 81	0900 19 MAR 81	214	1.1	4.4	5.366
25	No2 #25	1100 10 MAR 81	0700 30 MAR 81	276	.8	4.1	6.566
26	No2 #26	1100 10 MAR 81	0700 06 APR 81	644	4.3	3.5	13.584
27	No2 #27	1200 16 MAR 81	1100 19 MAR 81	071	-2.1	4.2	1.739
28	No2 #28	1200 16 MAR 81	0800 23 MAR 81	164	-.5	3.3	3.235
29	No2 #29	1200 16 MAR 81	0800 24 MAR 81	188	-.2	3.0	3.434
30	No2 #30	1200 16 MAR 81	0800 26 MAR 81	236	.6	3.7	4.016
31	No2 ST1	—	—	000	—	—	0.000
32	No2 ST2	—	—	000	—	—	0.000
33	No2 ST3	—	—	000	—	—	0.000

Table 1b Environmental Data For Prudhoe Bay Crude Oil.

#	SAMPLE	START TIME/DATE	END TIME/DATE	HOURS	AVERAGE TEMP DEG C	AVERAGE WIND M/SEC	EVAP EXPOSURE $X\ 10^{-6}$
01	PBC #01	1000 04 FEB 80	0900 05 FEB 80	024	-1.2	3.0	.449
02	PBC #02	1000 04 FEB 80	0900 06 FEB 80	048	-5.2	2.9	.337
03	PBC #03	1000 04 FEB 80	0900 08 FEB 80	096	-3.0	3.3	1.947
04	PBC #04	1000 04 FEB 80	0900 11 FEB 80	170	-2.2	3.0	3.138
05	PBC #05	1000 04 FEB 80	0900 19 FEB 80	360	-1.7	3.4	7.335
06	PBC #06	1000 04 FEB 80	0900 03 MAR 80	672	-1.4	3.2	13.071
07	PBC #07	1200 20 FEB 80	0900 21 FEB 80	021	3.2	1.1	.185
08	PBC #08	1200 20 FEB 80	1400 22 FEB 80	050	4.0	2.1	.707
09	PBC #09	1100 01 DEC 80	1000 02 DEC 80	023	-13.4	2.1	.320
10	PBC #10	1100 01 DEC 80	1000 03 DEC 80	047	-13.3	4.0	1.068
11	PBC #11	1400 06 JAN 81	1300 08 JAN 81	047	-3.3	4.1	1.134
12	PBC #12	1400 06 JAN 81	0800 10 JAN 81	090	-5.9	3.0	1.615
13	PBC #13	1400 06 JAN 81	0900 12 JAN 81	139	-8.1	3.2	2.730
14	PBC #14	1400 06 JAN 81	0900 15 JAN 81	211	-3.6	2.8	3.673
15	PBC #15	1400 06 JAN 81	1000 19 JAN 81	308	-7.5	2.8	5.450
16	PBC #16	1400 06 JAN 81	0900 22 JAN 81	379	-6.4	2.6	6.325
17	PBC #17	1400 06 JAN 81	0900 29 JAN 81	547	-4.3	2.6	9.090
18	PBC #18	1400 06 JAN 81	0900 04 FEB 81	691	-4.0	2.8	12.072
19	PBC #19	0900 03 FEB 81	0900 05 FEB 81	048	-8.2	3.0	.896
20	PBC #20	0900 03 FEB 81	0900 09 FEB 81	144	-3.7	2.9	2.631
21	PBC #21	0900 03 FEB 81	0900 12 FEB 81	216	-1.6	3.7	4.685
22	PBC #22	0900 03 FEB 81	0900 17 FEB 81	336	-1.6	3.2	6.474
23	PBC #23	0900 03 FEB 81	0900 19 FEB 81	384	-.7	3.1	7.189
24	PBC #24	0900 03 FEB 81	0900 23 FEB 81	480	1.0	3.3	9.418
25	PBC #25	0900 03 FEB 81	0900 26 FEB 81	552	1.6	3.3	10.926
26	PBC #26	0900 02 MAR 81	0900 04 MAR 81	048	-.4	3.4	1.011
27	PBC #27	0900 02 MAR 81	0900 09 MAR 81	168	1.0	2.9	3.042
28	PBC #28	0900 02 MAR 81	0900 12 MAR 81	240	1.5	2.8	4.250
29	PBC #29	0900 02 MAR 81	0900 16 MAR 81	336	1.8	3.5	7.071
30	PBC #30	0900 02 MAR 81	0900 19 MAR 81	408	1.2	3.7	8.329
31	PBC #31	1100 10 MAR 81	0900 23 MAR 81	310	1.0	3.8	6.895
32	PBC #32	1100 10 MAR 81	0700 26 MAR 81	380	1.4	3.4	7.651
33	PBC #33	1100 10 MAR 81	0700 30 MAR 81	476	2.3	3.4	9.713
34	PBC #34	1100 10 MAR 81	0800 06 APR 81	645	4.3	3.5	13.605
35	PBC #35	1100 10 MAR 81	0700 13 APR 81	811	5.1	3.6	17.443
36	PBC ST1	---	---	000	---	---	0.000
37	PBC ST2	---	---	000	---	---	0.000
38	PBC ST3	---	---	000	---	---	0.000

Table 1c Environmental Data For No.4 Fuel Oil.

#	SAMPLE	START TIME/DATE	END TIME/DATE	HOURS	AVERAGE TEMP DEG C	AVERAGE WIND M/SEC	EVAP EXPOSURE X 10^{-6}
01	No4 #01	1300 18 FEB 80	1300 19 FEB 80	022	.4	5.3	.645
02	No4 #02	1300 18 FEB 80	0900 20 FEB 80	042	.8	3.7	.906
03	No4 #03	1300 18 FEB 80	1200 22 FEB 80	093	2.8	2.7	1.579
04	No4 #04	1300 18 FEB 80	1400 25 FEB 80	167	3.0	2.5	2.677
05	No4 #05	1400 03 MAR 80	0900 05 MAR 80	043	2.1	3.0	.784
06	No4 #06	1400 03 MAR 80	1500 06 MAR 80	073	3.2	3.4	1.493
07	No4 #07	1400 06 JAN 81	1300 07 JAN 81	023	.4	4.0	.547
08	No4 #08	1400 06 JAN 81	0800 10 JAN 81	090	-5.9	3.0	1.645
09	No4 #09	1400 06 JAN 81	0900 12 JAN 81	139	-8.1	3.2	2.730
10	No4 #10	1400 06 JAN 81	0900 15 JAN 81	211	-8.6	2.8	3.693
11	No4 #11	1400 06 JAN 81	1000 19 JAN 81	308	-7.5	2.8	5.450
12	No4 #12	1400 06 JAN 81	0900 22 JAN 81	379	-6.4	2.6	6.325
13	No4 #13	1400 06 JAN 81	0900 29 JAN 81	547	-4.3	2.6	9.090
14	No4 #14	1400 06 JAN 81	0900 04 FEB 81	691	-4.0	2.8	12.072
15	No4 #15	0900 03 FEB 81	0900 05 FEB 81	048	-8.2	3.0	.396
16	No4 #16	0900 03 FEB 81	0900 09 FEB 81	144	-3.7	2.9	2.631
17	No4 #17	0900 03 FEB 81	0900 12 FEB 81	216	-1.6	3.7	4.685
18	No4 #18	0900 03 FEB 81	0900 17 FEB 81	336	-1.6	3.2	6.494
19	No4 #19	0900 03 FEB 81	0900 19 FEB 81	384	-.7	3.1	7.189
20	No4 #20	0900 03 FEB 81	0900 23 FEB 81	480	1.0	1.5	9.418
21	No4 #21	0900 03 FEB 81	0900 26 FEB 81	552	1.6	3.3	10.926
22	No4 #22	0900 02 MAR 81	0800 04 MAR 81	048	-.4	3.4	1.011
23	No4 #23	0900 02 MAR 81	0900 09 MAR 81	168	1.0	2.9	3.042
24	No4 #24	0900 02 MAR 81	0900 12 MAR 81	240	1.5	2.8	4.250
25	No4 #25	0900 02 MAR 81	0900 16 MAR 81	336	1.8	3.5	7.071
26	No4 #26	0900 02 MAR 81	0800 19 MAR 81	408	1.2	3.7	8.829
27	No4 #27	1100 10 MAR 81	0800 23 MAR 81	310	1.0	3.8	6.395
28	No4 #28	1100 10 MAR 81	0700 26 MAR 81	380	1.4	3.4	7.651
29	No4 #29	1100 10 MAR 81	0700 30 MAR 81	476	2.3	3.4	9.713
30	No4 #30	1100 10 MAR 81	0800 06 APR 81	645	4.3	3.5	13.605
31	No4 #31	1100 10 MAR 81	0700 13 APR 81	811	5.1	3.6	17.443
32	No4 ST1	---	---	000	---	---	0.000
33	No4 ST2	---	---	000	---	---	0.000
34	No4 ST3	---	---	000	---	---	0.000

Table 1d Environmental Data For No.6 Fuel Oil.

#	SAMPLE	START TIME/DATE	END TIME/DATE	HOURS	AVERAGE TEMP DEG C	AVERAGE WIND M/SEC	EVAP EXPOSURE X 10^{-6}
01	N06 #01	1100 08 DEC 80	0900 09 DEC 80	022	9.5	4.0	.028
02	N06 #02	1100 08 DEC 80	0900 10 DEC 80	046	6.9	3.0	.047
03	N06 #03	1100 08 DEC 80	0900 12 DEC 80	094	2.9	3.0	.076
04	N06 #04	1100 08 DEC 80	1600 15 DEC 80	173	1.5	3.6	.202
05	N06 #05	1100 08 DEC 80	0900 18 DEC 80	238	.7	3.4	.265
06	N06 #06	1100 08 DEC 80	0900 22 DEC 80	334	-.8	3.4	.379
07	N06 #07	1600 12 JAN 81	0800 14 JAN 81	040	-11.5	2.4	.035
08	N06 #08	1600 12 JAN 81	0900 16 JAN 81	089	-8.2	2.1	.071
09	N06 #09	1600 12 JAN 81	1400 19 JAN 81	166	-6.6	2.6	.151
10	N06 #10	1600 12 JAN 81	0900 22 JAN 81	233	-5.3	2.3	.192
11	N06 #11	1600 12 JAN 81	0800 26 JAN 81	328	-3.9	2.4	.278
12	N06 #12	1600 12 JAN 81	0900 04 FEB 81	545	-2.9	2.7	.508
13	N06 #13	1600 12 JAN 81	0900 11 FEB 81	713	-2.7	2.9	.695
14	STD #01	---	---	000	---	---	0.000

These groupings delineate general overall conditions under which the various samples weathered. For instance, the Winter 1980 group specifies samples that were weathered during cold weather in February-March 1980 when the ice blocks were generally intact and air temperatures were generally below freezing. In addition, these samples were covered with the transparent covers to protect them from precipitation. These samples were also initially deposited in cavities in the ice so that the spill area was generally less than the box area for the first few days. Although these samples started out on a solid ice surface, by the end of the period some melting had occurred so that a simulated melt pond situation existed.

The Winter 1981 group contains those samples which were weathered during very cold weather in January 1981. These samples were weathered for the most part on a solid ice surface, and were not initially deposited in a cavity so that the oil covered the major portion of the box area. In addition, the samples were not sheltered by the plastic screens so that snow was allowed to accumulate on the samples. This led to some interesting observations of oil/snow/ice interaction for the darker oils (No. 4 and Prudhoe Bay crude) as solar radiation and warmer temperatures melted the snow. It appears that the darker oils will initially be sheltered from the atmosphere by the snow as shown in Figure 5a. As solar radiation warms the snow and the oil underneath, the oil appears to pocket in small depressions in the snow and ice (up to a few centimeters in diameter) as shown in Figures 5b and 5c. It is quite possible that this initial sheltering followed by the collection of the oil into small pockets with a local increase in slick thickness, may have a significant short-term effect on the weathering rate. The lighter No. 2 home heating oil did not show this pocketing tendency, but rather saturated the snow evenly shortly after being covered.

The third group of samples, Winter 1981 (emulsified), refers primarily to those samples that were weathered during February 1981. These samples were placed on the ice during a warming period in February 1981. The samples were deposited in 30 cm x 30 cm cavities in the ice to prevent runoff, but were not covered with the transparent screens. Melt pond conditions prevailed throughout the period. During the night of 7-8 February, heavy rains fell inundating the samples. Although the samples remained intact with little oil loss, some oil emulsification was immediately noticed. As will be shown later in this report, the emulsification significantly affected the physical properties and possibly the weathering rates of the samples. Accordingly, some of the later samples (March-April 1981) which showed indications of emulsification are also included in this group.

The fourth group (Spring 1981) refers to those samples that were weathered during March-April 1981 when warmer weather prevailed (daytime temperatures well above $0^{o}C$), and clear skies led to significant solar radiation levels at the test site. As periods of melting and rainfall were expected, the samples were deposited in the 30 cm x 30 cm cavities, and covered with the transparent screens. These samples generally experienced a progression of underlying surface conditions as the ice blocks deteriorated. The samples would rest on solid ice for the first day or so, spread out as melt water created a melt pool situation after a few days, and eventually weather in open water about 20-30 cm deep as the ice block deteriorated completely. This hopefully simulated late summer conditions on the North Slope when accelerated weathering of a spill is likely to occur.

The No. 6 fuel oil samples were not separated into groups, and were analyzed in only a cursory fashion, as very little weathering was observed for this type of oil. In fact, the No. 6 oil congealed into a semi-solid mass at the colder ambient temperatures on the roof, and did not spread into a slick as did the other oils. When periods of warmer temperatures and increased solar radiation melted the ice around the oil, this semi-solid mass would become partially submerged in the melt water. If the melt water refroze, the oil mass would then be largely encapsulated in the ice, further sheltering the oil from the atmosphere. Mass fraction remaining and density values for these samples confirmed the absence of any appreciable weathering.

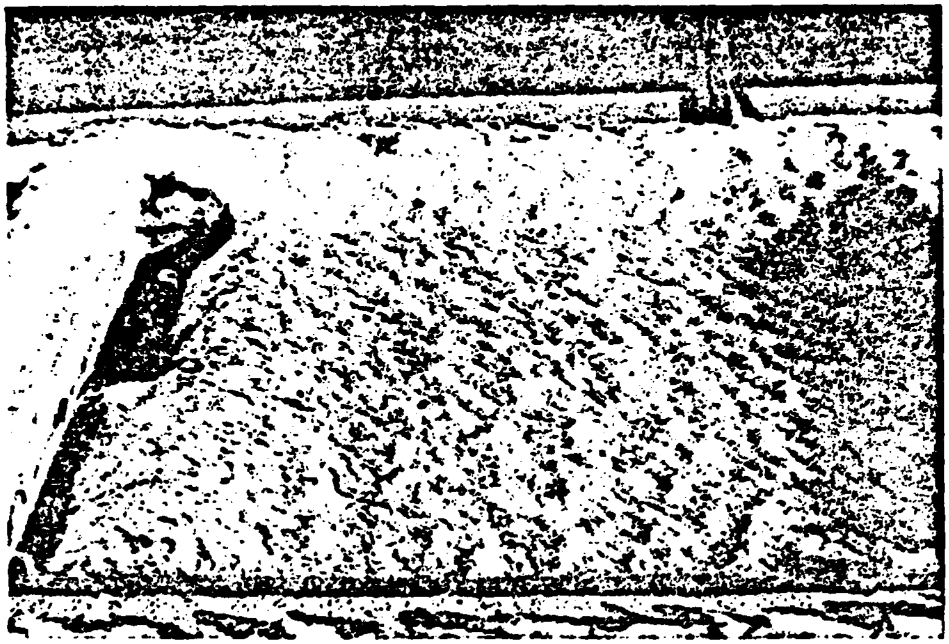

Figure 5a Photograph Showing Dark Oil Sample Covered by a Layer of Snow.

Figure 5b Photograph Showing Dark Oil Sample After Snow Layer Has Melted.

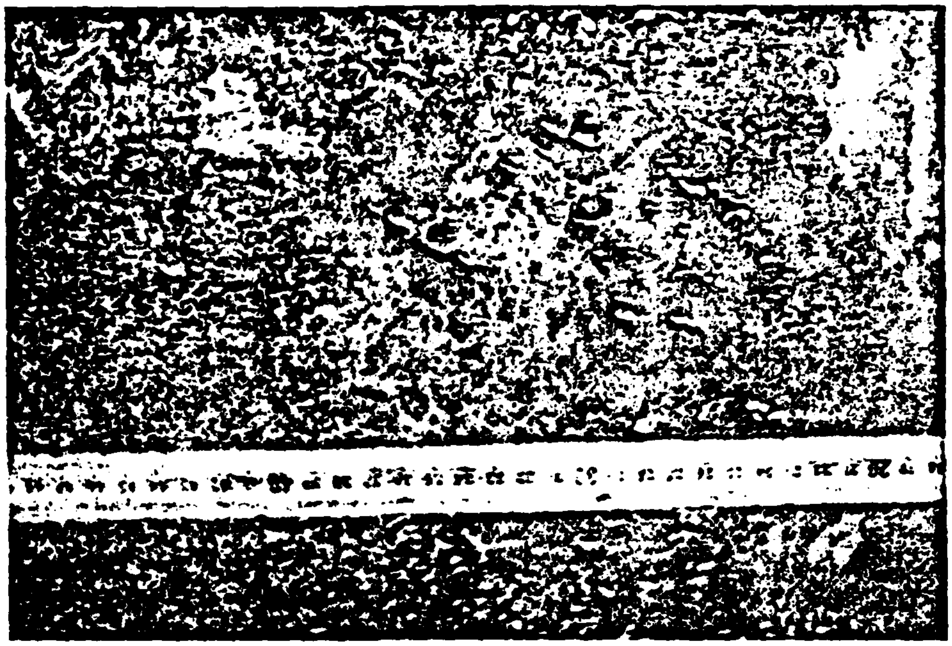

Figure 5c Photograph Showing Closeup of Dark Oil Sample with Oil Pockets (Scale in Centimeters).

6.2 Change in Mass and Physical Properties

A complete tabulation of the mass fraction remaining and physical properties values obtained from the sample analysis is given in Tables 2a-2d and 3a-3c. Figures 6 through 14 contain plots of the mass fraction remaining and various physical properties vs. the cumulative evaporative exposure. The following discussion highlights the important trends and significant processess involved in the change of these parameters during weathering.

Table 2a Mass Fraction Remaining and Physical Properties (Density, Oil/Water Interfacial Tension, and Aqueous Solubility) for No.2 Heating Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	MASS FRACTION	DENSITY 0 DEG C G/CM^3	DENSITY 20 DEG C G/CM^3	DENSITY 25 DEG C G/CM^3	OIL/WATER 20 DEG C DYNE/CM	SOLUBILITY 20 DEG C G/M^3
01	NO2 #01	.559	.80	----	----	.884	----	- - - -
02	NO2 #02	1.021	----	----	----	----	----	----
03	NO2 #03	2.105	.82	----	----	.888	----	- - -
04	NO2 #04	3.582	.74	----	----	.859	----	----
05	NO2 #05	6.219	.39	----	----	.857	----	- - -
06	NO2 #06	0.000	----	----	----	----	----	----
07	NO2 #07	.278	.77	----	----	.858	----	- - -
08	NO2 #08	.547	.40	.856	.845	.829	3.5	.73
09	NO2 #09	1.645	.22	----	----	.831	----	- - -
10	NO2 #10	2.730	.56	----	----	.832	----	----
11	NO2 #11	3.693	.34	----	----	.831	----	- - -
12	NO2 #12	5.450	.04	----	----	.832	----	----
13	NO2 #13	6.325	.20	----	----	----	----	- - -
14	NO2 #14	9.090	.39	----	----	.832	----	----
15	NO2 #15	12.072	.06	----	----	----	----	- - -
16	NO2 #16	.896	.82	.855	.843	.827	4.6	.87
17	NO2 #17	2.631	.05	----	----	.833	----	- - - -
18	NO2 #18	.200	.64	----	----	.825	----	----
19	NO2 #19	.305	.71	.853	.841	.826	20.2	1.42
20	NO2 #20	.787	.76	.855	.843	.828	2.9	.76
21	NO2 #21	2.250	.79	----	----	.830	----	- - -
22	NO2 #22	3.633	.59	----	----	.833	----	----
23	NO2 #23	4.951	.03	----	----	----	----	- - -
24	NO2 #24	5.366	.54	----	----	.833	----	----
25	NO2 #25	6.566	.42	.861	.848	.835	4.0	.21
26	NO2 #26	13.584	.25	----	----	.837	----	----
27	NO2 #27	1.739	.70	.856	.845	.827	4.3	.75
28	NO2 #28	3.235	.82	.859	.846	.831	4.3	.31
29	NO2 #29	3.484	.76	----	----	.832	----	- - -
30	NO2 #30	4.016	.77	.858	.848	.833	4.4	.28
31	NO2 ST1	0.000	----	----	----	.832	----	- - -
32	NO2 ST2	0.000	----	.849	.840	.824	25.6	3.12
33	NO2 ST3	0.000	----	----	----	.825	----	- - -

Table 2b Mass Fraction Remaining and Physical Properties (Density, Oil/Water Interfacial Tension, and Aqueous Solubility) for Prudhoe Bay Crude Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	MASS FRACTION	DENSITY 0 DEG C G/CM^3	DENSITY 20 DEG C G/CM^3	DENSITY 25 DEG C G/CM^3	OIL/WATER 20 DEG C DYNE/CM	SOLUBILITY 20 DEG C G/M^3
01	PBC #01	.449	.90	—	—	—	—	—
02	PBC #02	.887	.91	—	—	—	—	-.-
03	PBC #03	1.947	.91	—	—	.918	—	—
04	PBC #04	3.188	.87	—	—	.926	—	-.-
05	PBC #05	7.335	.84	—	—	.930	—	—
06	PBC #06	13.071	.57	—	—	.938	—	-.-
07	PBC #07	.185	.92	—	—	.915	—	—
08	PBC #08	.707	.94	—	—	.924	—	-.-
09	PBC #09	.320	.88	—	—	.911	—	—
10	PBC #10	1.068	.75	—	—	.926	—	-.-
11	PBC #11	1.134	.41	—	—	.923	—	—
12	PBC #12	1.645	.66	.936	.931	.923	10.8	4.28
13	PBC #13	2.730	.98	—	—	.910	—	—
14	PBC #14	3.693	.70	—	—	.914	—	-.-
15	PBC #15	5.450	.61	—	—	.920	—	—
16	PBC #16	6.325	.72	—	—	.918	—	-.-
17	PBC #17	9.090	.84	—	—	.922	—	—
18	PBC #18	12.072	1.04	—	—	.927	—	-.-
19	PBC #19	.896	.96	.934	.920	.905	10.1	8.50
20	PBC #20	2.631	.94	—	—	.914	—	-.-
21	PBC #21	4.685	1.75	.976	.969	.963	—	.53
22	PBC #22	6.494	1.16	.983	.977	.970	—	.30
23	PBC #23	7.189	1.50	—	—	.966	—	—
24	PBC #24	9.418	1.76	.989	.981	.973	—	.15
25	PBC #25	10.926	1.32	—	—	.970	—	—
26	PBC #26	1.011	.69	—	—	.910	—	-.-
27	PBC #27	3.042	.47	.944	.933	.917	1.7	1.93
28	PBC #28	4.250	.81	—	—	.920	—	-.-
29	PBC #29	7.071	.76	.968	.960	.934	—	.18
30	PBC #30	8.829	.58	—	—	.943	—	-.-
31	PBC #31	6.895	.85	—	—	.929	—	—
32	PBC #32	7.651	.75	—	—	.931	—	-.-
33	PBC #33	9.713	.74	—	—	.935	—	—
34	PBC #34	13.605	1.23	—	—	.963	—	-.-
35	PBC #35	17.443	1.29	.987	.980	.967	—	.04
36	PBC ST1	0.000	—	—	—	.899	—	-.-
37	PBC ST2	0.000	—	.989	.981	.884	27.0	29.20
38	PBC ST3	0.000	—	—	—	.884	—	-.-

Table 2c Mass Fraction Remaining and Physical Properties (Density, Oil/Water Interfacial Tension, and Aqueous Solubility) for No.4 Fuel Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	MASS FRACTION	DENSITY 0 DEG C G/CM^3	DENSITY 20 DEG C G/CM^3	DENSITY 25 DEG C G/CM^3	OIL/WATER 20 DEG C DYNE/CM	SOLUBILITY 20 DEG C G/M^3
01	NO4 #01	.645	.86	----	----	.916	----	----
02	NO4 #02	.906	.30	----	----	.918	----	----
03	NO4 #03	1.579	.94	----	----	.919	----	----
04	NO4 #04	2.677	1.07	----	----	.924	----	----
05	NO4 #05	.784	.70	----	----	.897	----	----
06	NO4 #06	1.493	.94	----	----	.900	----	----
07	NO4 #07	.547	.64	.943	.932	.913	22.3	4.22
08	NO4 #08	1.645	.84	----	----	.921	----	----
09	NO4 #09	2.730	.96	----	----	.917	----	----
10	NO4 #10	3.693	.60	.960	.945	.924	24.5	2.58
11	NO4 #11	5.450	1.13	----	----	.927	----	----
12	NO4 #12	6.325	.84	.960	.951	.927	24.8	1.74
13	NO4 #13	9.090	.75	----	----	.933	----	----
14	NO4 #14	12.072	.72	.978	.970	.956	----	.69
15	NO4 #15	.896	1.20	----	----	.912	----	----
16	NO4 #16	2.631	1.42	.954	.941	.931	23.6	1.43
17	NO4 #17	4.685	1.28	----	----	.970	----	----
18	NO4 #18	6.494	1.31	----	----	.974	----	----
19	NO4 #19	7.189	1.69	----	----	.976	----	----
20	NO4 #20	9.418	1.49	.990	.979	.959	----	.25
21	NO4 #21	10.926	1.22	----	----	.949	----	----
22	NO4 #22	1.011	.92	.945	.934	.919	30.1	2.49
23	NO4 #23	3.042	1.02	----	----	.920	----	----
24	NO4 #24	4.250	1.02	----	----	.930	----	----
25	NO4 #25	7.071	1.64	----	----	.974	----	----
26	NO4 #26	8.829	1.30	----	----	.968	----	----
27	NO4 #27	6.895	1.71	----	----	.969	----	----
28	NO4 #28	7.651	1.32	----	----	.967	----	----
29	NO4 #29	9.713	1.54	----	----	.969	----	----
30	NO4 #30	13.605	1.29	.992	.984	.969	----	.20
31	NO4 #31	17.443	1.18	----	----	.952	----	----
32	NO4 ST1	0.000	----	----	----	.915	----	----
33	NO4 ST2	0.000	----	.938	.925	.910	30.2	6.46
34	NO4 ST3	0.000	----	----	----	.910	----	----

Table 2d Mass Fraction Remaining and Density for No.6 Fuel Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	MASS FRACTION	DENSITY 25 DEG C G/CM^3
01	NO6 #01	.028	----	.916
02	NO6 #02	.047	----	.915
03	NO6 #03	.096	----	.915
04	NO6 #04	.202	----	.915
05	NO6 #05	.265	----	.915
06	NO6 #06	.379	----	.917
07	NO6 #07	.035	.97	.914
08	NO6 #08	.071	.90	.914
09	NO6 #09	.151	.86	.914
10	NO6 #10	.192	.90	.917
11	NO6 #11	.278	.81	.917
12	NO6 #12	.508	.80	.915
13	NO6 #13	.695	.83	.916
14	NO6 #14	0.000	----	.914

Mass Fraction Remaining

The mass fraction remaining values for all four types of oil are given in Tables 2a through 2d. Mass fraction remaining vs. evaporative exposure is plotted in Figures 6a through 6c for the No. 2 oil, No. 4 oil, and Prudhoe Bay crude. All data points, except for the emulsified samples, are included in these plots, with each data point identified as to which sample group it belongs to. All three plots show a good deal of scatter due to the inaccuracies in the measurement procedure outlined in Appendix B. To facilitate limited interpretation of the data, a maximum mass fraction remaining envelope has been drawn above the points. As expected, No. 2 home heating oil shows the greatest mass loss (75% after 20 days), followed by Prudhoe Bay crude (45% after 1 month), and No. 4 fuel oil (28% after 1 month). The plots further suggest that Prudhoe Bay crude and No. 4 fuel oil evaporate at a more or less constant rate until a limiting value is reached. In contrast, the No. 2 home heating oil appears to undergo accelerated evaporation between evaporative exposure values of $4x10^6$ and $6x10^6$. However, there is no theoretical explanation for this accelerated evaporation, and it may in fact be due to inaccuracies in the measurement procedures. There is no mass fraction remaining plot for the No. 6 fuel oil, as the values in Table 2d (samples 7-13) indicate little or no change as expected. In summary, Figures 6a through 6c show no well-defined functional relationship between mass fraction remaining and evaporative exposure. However, this is undoubtedly due largely to inaccuracies in the sample analysis which obscures any quantitative relation between the two parameters.

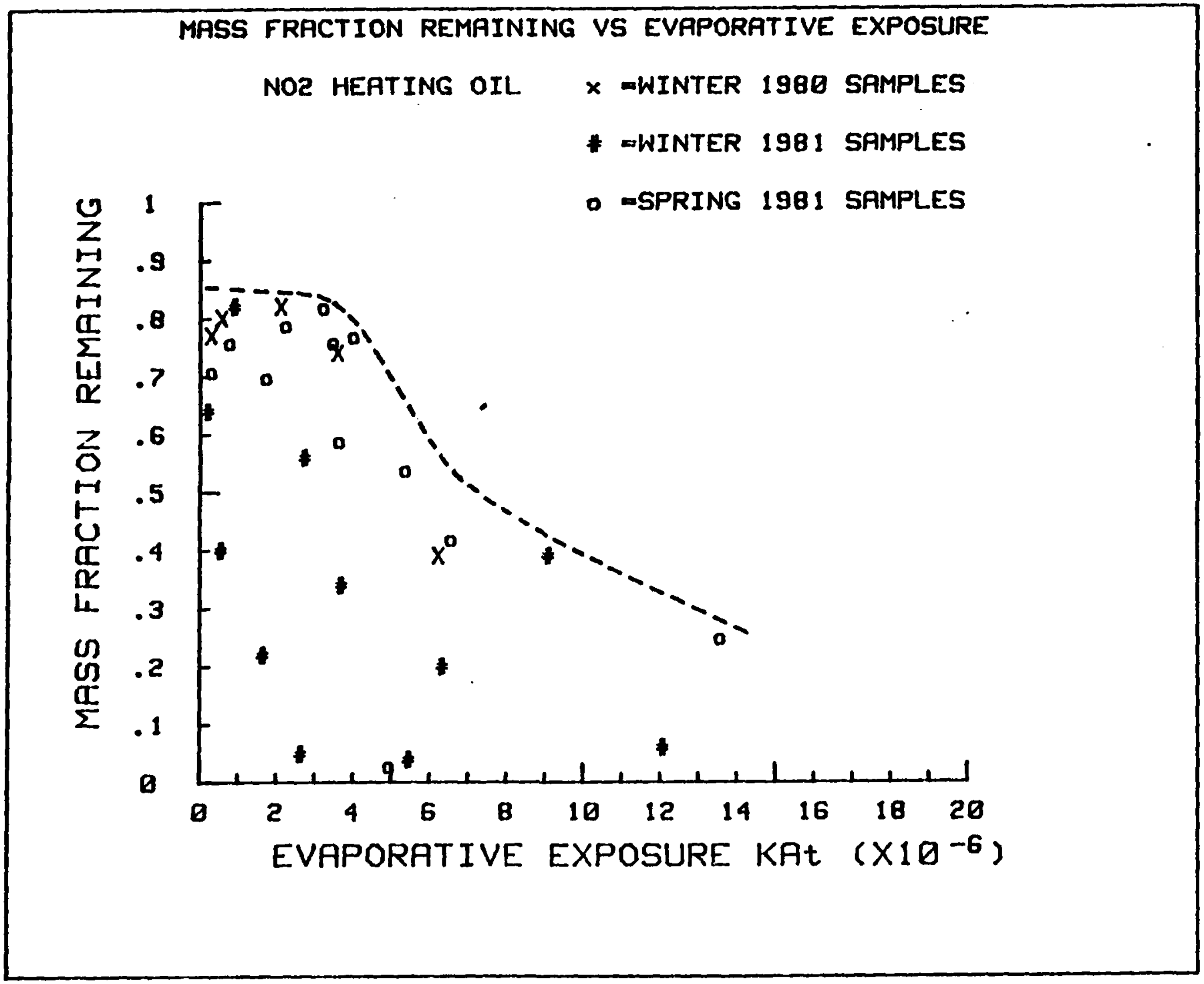

Figure 6a Mass Fraction Remaining vs. Evaporative Exposure for No. 2 Heating Oil.

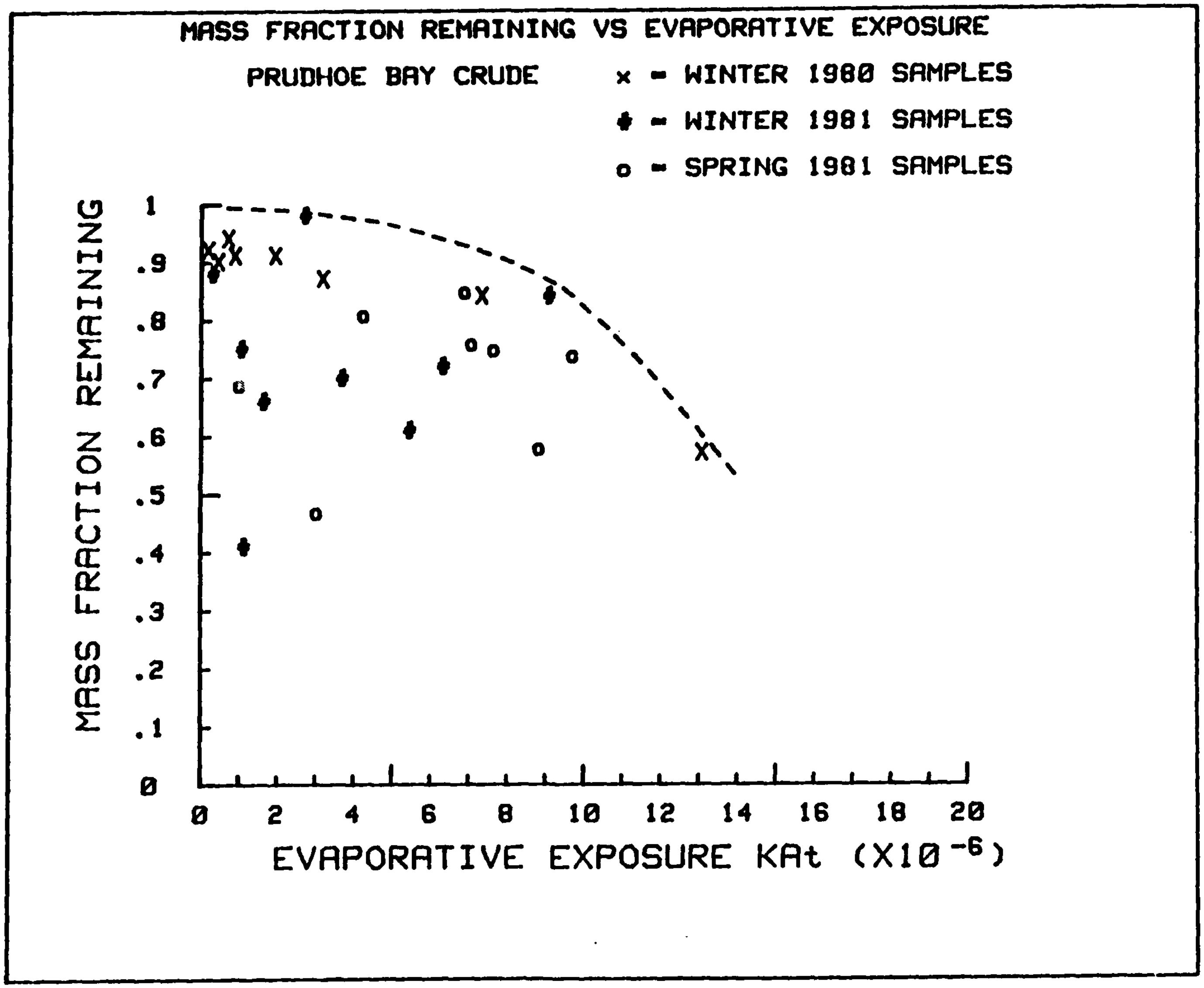

Figure 6b Mass Fraction Remaining vs. Evaporative Exposure for Prudhoe Bay Crude Oil.

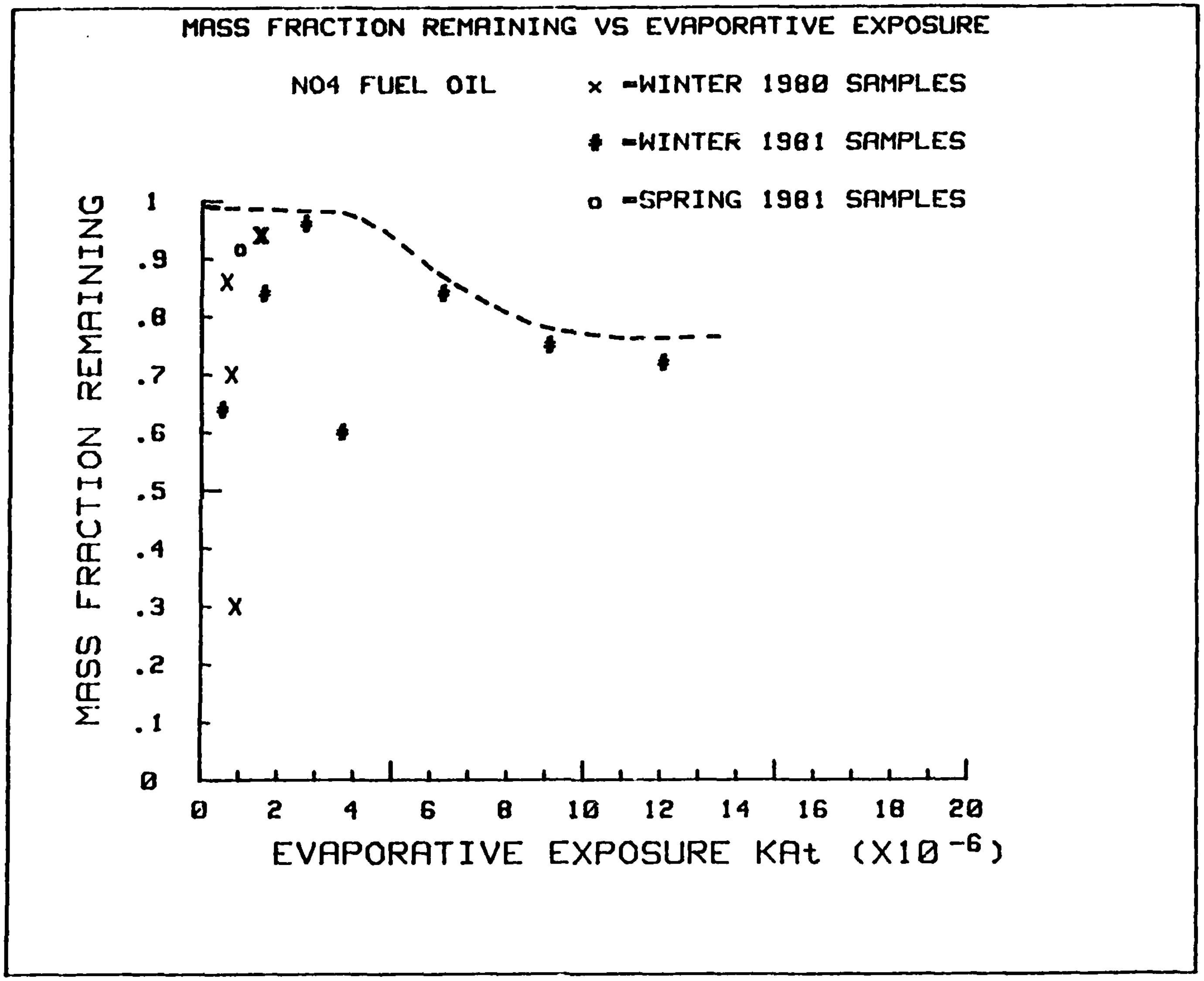

Figure 6c Mass Fraction Remaining vs. Evaporative Exposure for No. 4 Fuel Oil.

Density

The various density values (0°C, 20°C, 25°C) for all four types of oil are given in Tables 2a through 2d. Plots of density at 25°C vs. evaporative exposure using all the values obtained at the R&D Center are shown in Figures 7a through 7c for the No. 2 heating oil, No. 4 fuel oil, and Prudhoe Bay crude. In general, all three of these plots show an increase in density over the weathering period, following a general linear trend. The density of No. 2 home heating oil increases only slightly from 0.825 g/cm^3 to 0.838 g/cm^3 after roughly one month. The change is somewhat more significant for Prudhoe Bay crude, from 0.887 g/cm^3 to about 0.94 g/cm^3 after a month. Likewise, the density of No. 4 fuel oil changes significantly from 0.913 g/cm^3 to about 0.96 g/cm^3 after a month. It is clear for the Prudhoe Bay crude and No. 4 fuel oil that departures from this trend and range of density values are primarily due to emulsification. During this experiment, emulsification produced Prudhoe Bay crude and No. 4 fuel oil densities of almost 0.98 g/cm^3. Figure 7a also shows similar departures for the No. 2 heating oil samples from the Winter 1980 group. Emulsification is again suspected for these samples, although no clear evidence of this was noted in the sample analysis. With regard to the No. 6 fuel oil, Table 2d clearly indicates little or no change in the density values with weathering, and for this reason no plot was made.

Figures 8a through 8c show the density values at 0°C and 20°C plotted against evaporative exposure for the No. 2 heating oil, No. 4 fuel oil, and Prudhoe Bay crude. These values were obtained through sample analysis conducted by the University of Toronto. These plots confirm the increase in density with weathering as discussed above. The data points for the emulsified samples have been circled, again showing the effect of emulsification on increasing the oil density.

This increase in density with evaporation and emulsification is significant primarily for the Prudhoe Bay crude and No. 4 fuel oil, in that these weathering processes can increase the density of the oil to values approaching 1.0 g/cm^3. With the density of seawater generally below 1.035 g/cm^3 and with a layer of fresh water on the surface during spring runoff, this may have important effects on the vertical location and movement of oil in sea ice, which has a typical density of 0.91 g/cm^3. With regard to modelling this density increase, the plots show a functional dependence of density on evaporative exposure for cases where emulsification is not a factor. However, emulsification can increase the density of the oil significantly, independent of the evaporative exposure levels. This may complicate efforts to model the change in density under actual spill conditions.

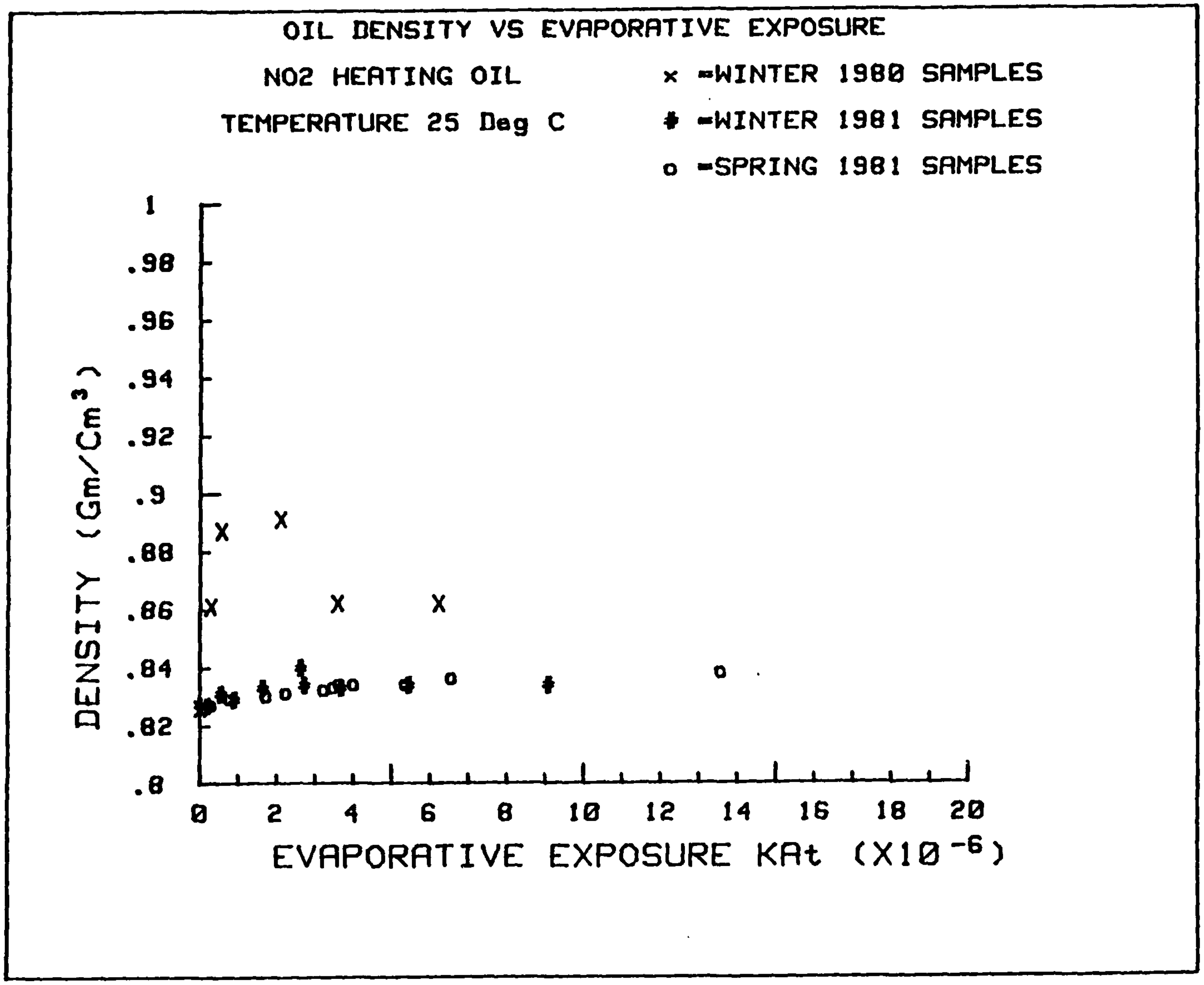

Figure 7a Density (at 25^{0} C) vs. Evaporative Exposure for No. 2 Heating Oil.

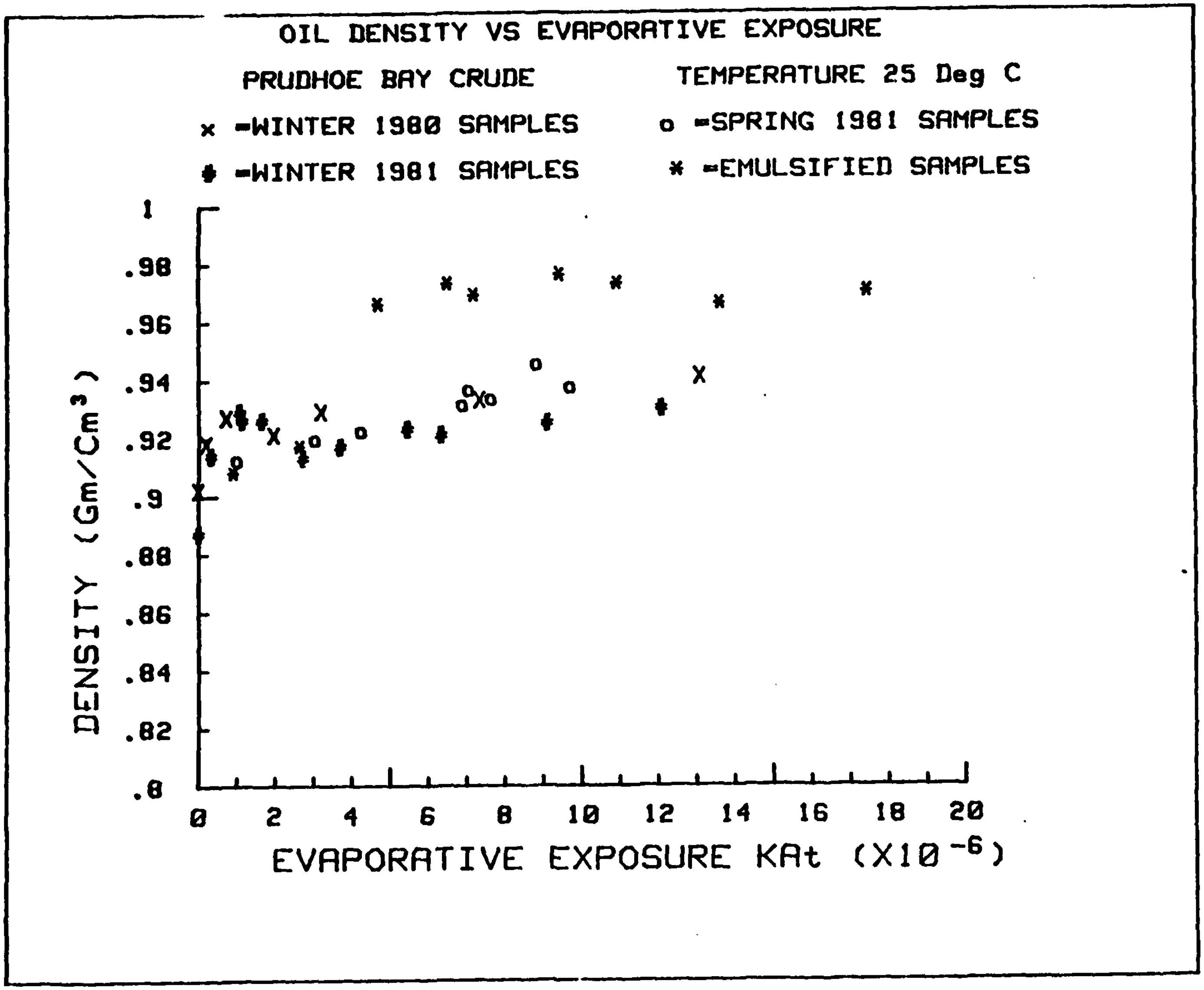

Figure 7b Density (at 25^0 C) vs. Evaporative Exposure for Prudhoe Bay Crude Oil.

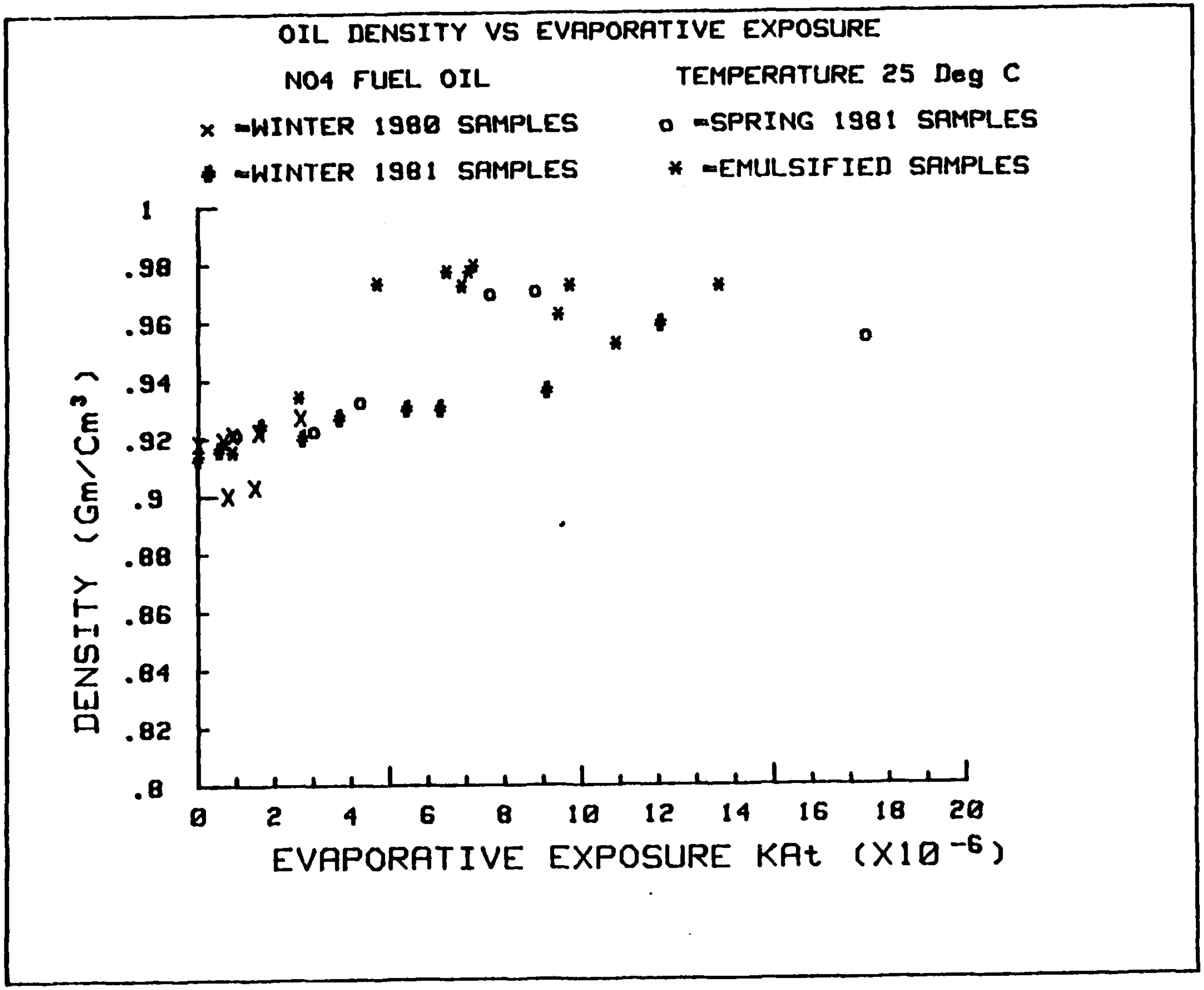

Figure 7c Density (at 25° C) vs. Evaporative Exposure for No. 4 Fuel Oil.

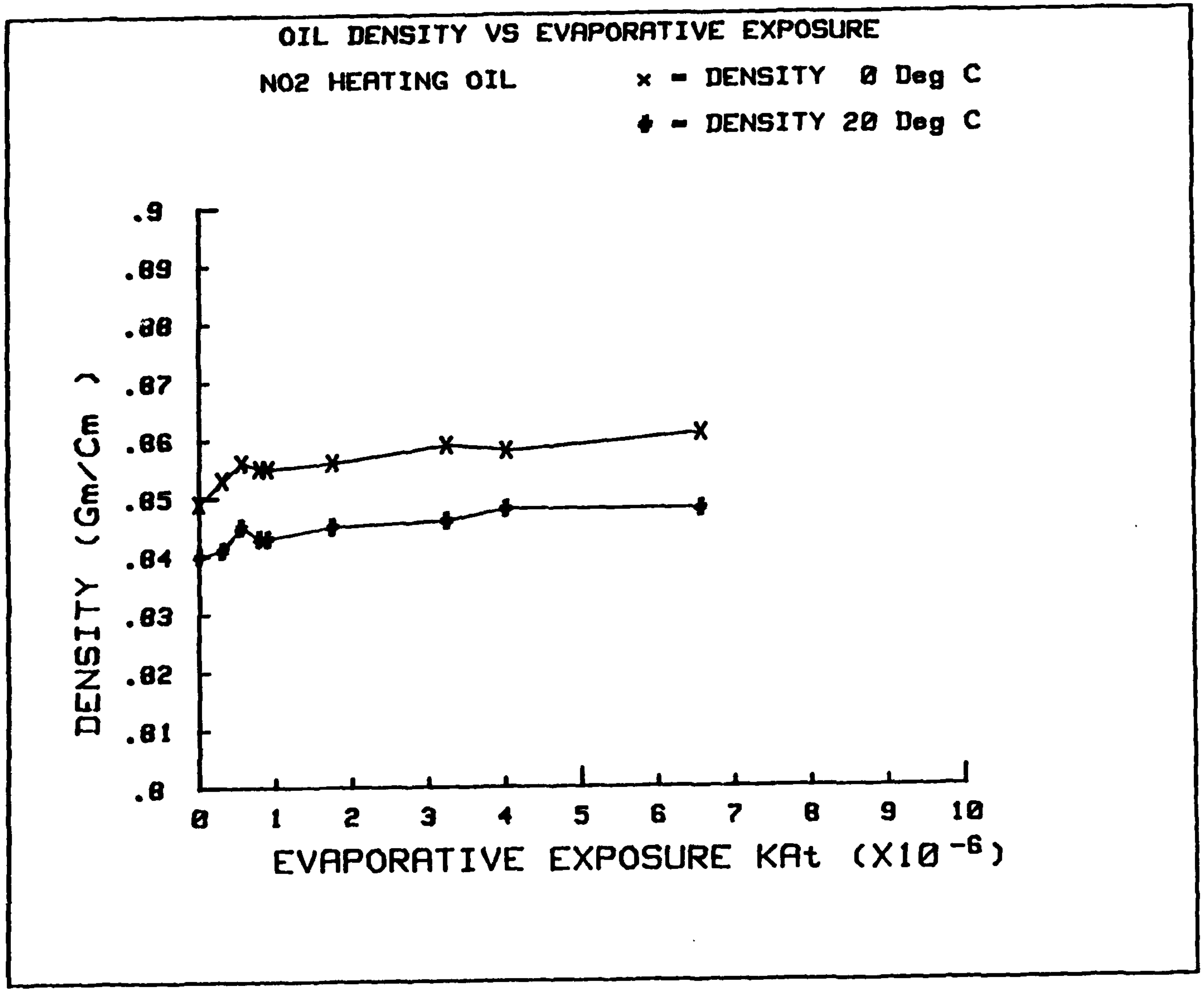

Figure 8a Density (at 0^0 and 20^0 C) vs. Evaporative Exposure for No. 2 Heating Oil.

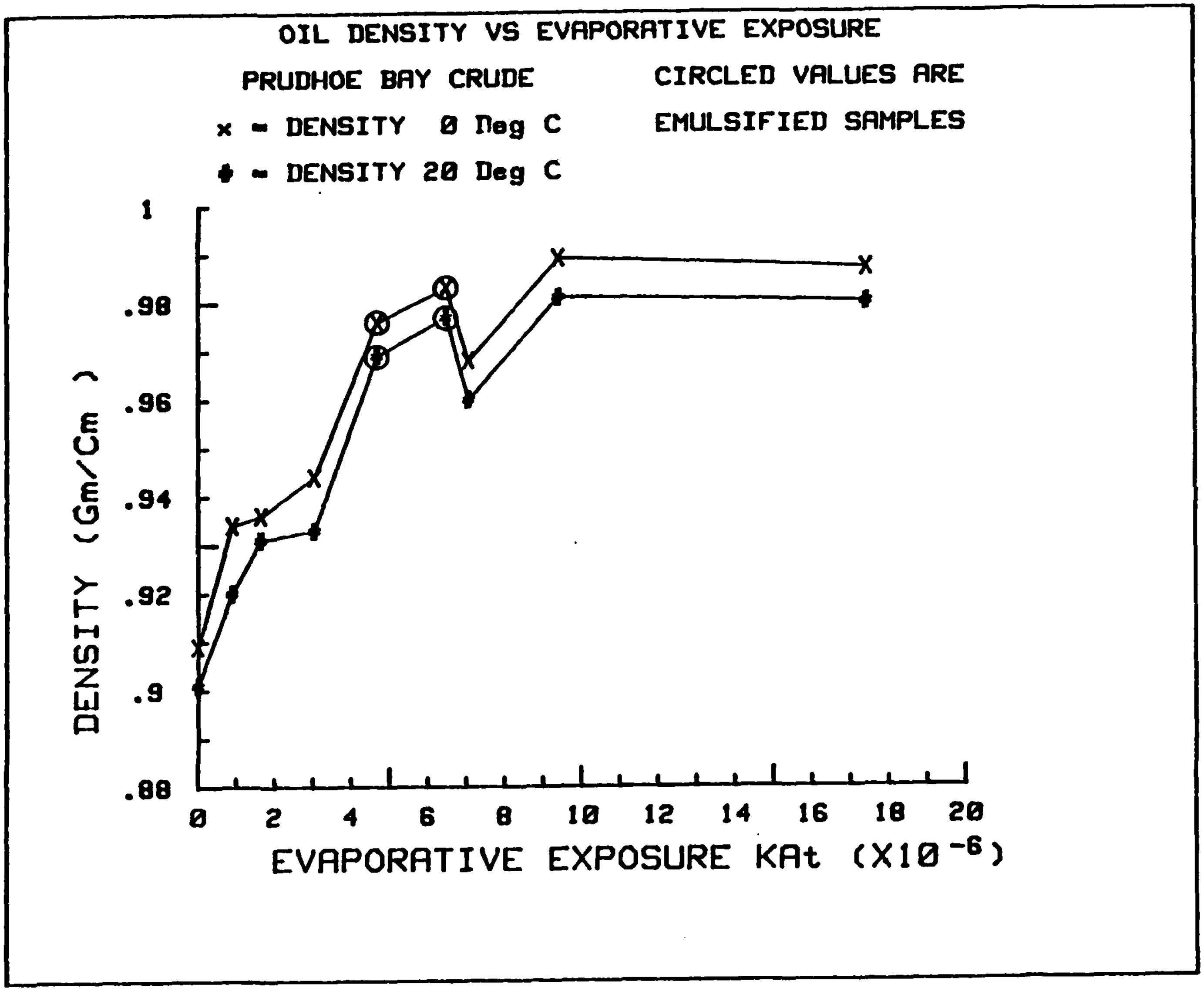

Figure 8b Density (at 0^{0} and 20^{0} C) vs. Evaporative Exposure for Prudhoe Bay Crude Oil.

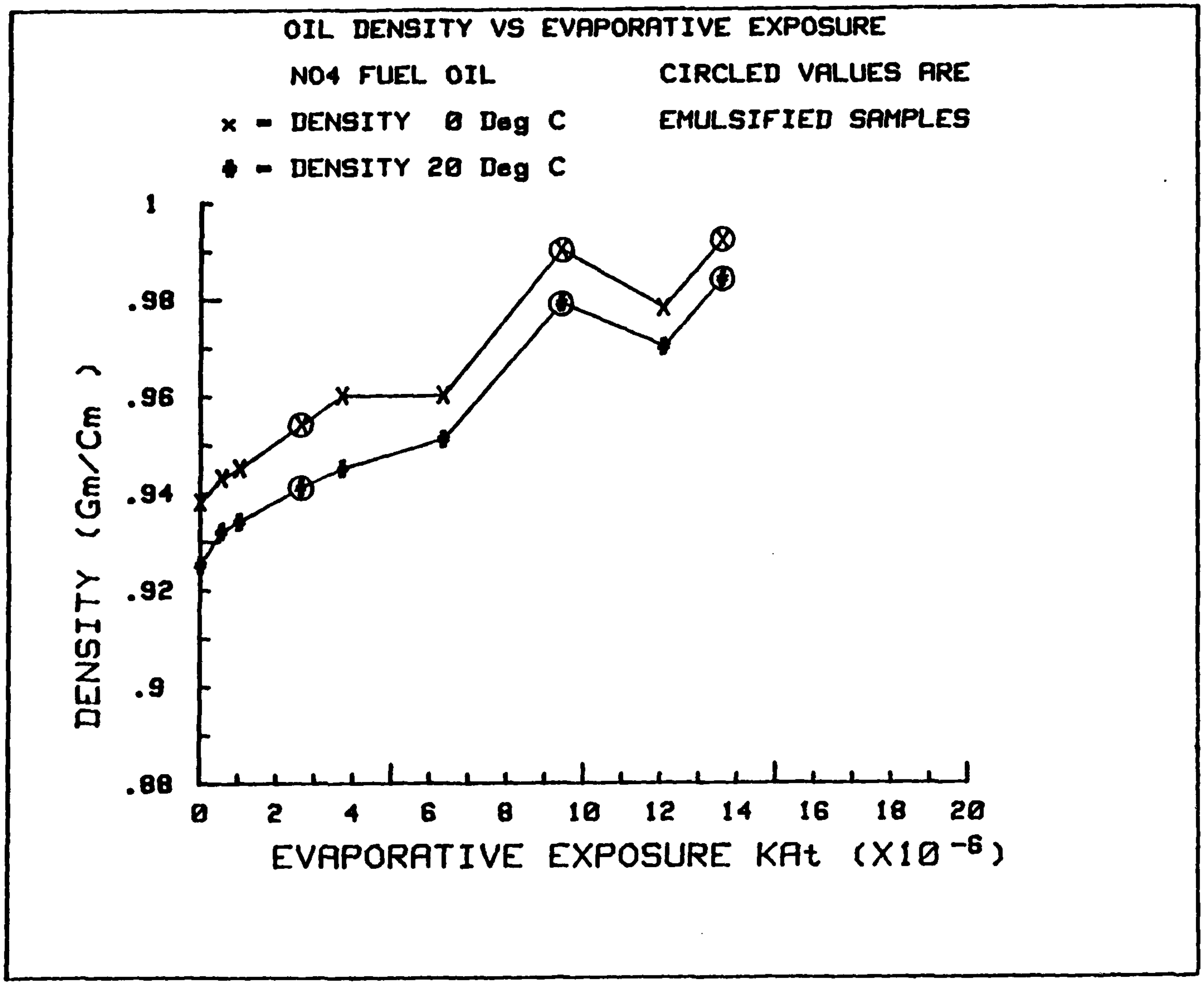

Figure 8c Density (at 0^{0} and 20^{0} C) vs. Evaporative Exposure for No. 4 Fuel Oil.

Oil-Water Interfacial Tension

Values of oil/water interfacial tension for selected No. 2 heating oil, No. 4 fuel oil, and Prudhoe Bay crude samples are tabulated in Tables 2a through 2c. Plots of these values vs. evaporative exposure are given in Figure 9 for all three oils. The interfacial tension of the No. 2 heating oil decreases rapidly with weathering from an initial value of 25.6 dyne/cm to about 4 dyne/cm after a week of exposure. Likewise, the interfacial tension of the Prudhoe Bay crude decreases from an initial value of 27.0 dyne/cm to 1.7 dyne/cm within a week. The decrease in interfacial tension for the No. 4 fuel oil is far less significant, from 30.2 dyne/cm to about 24 dyne/cm after two weeks. The plots for interfacial tension do not show a well-defined quantitative dependence on the evaporative exposure levels.

Changes in interfacial tension have important implications in the vertical and horizontal movement of oil in an ice-infested environment. Various researchers have documented the importance of surface tension in controlling the equilibrium thickness of an oil spill in open water (Fazal and Milgram, 1977), and both on the surface and underneath a smooth solid ice sheet (Cox et al., 1980). In addition, Free et al. (1981) have investigated the importance of interfacial tension in controlling the horizontal seepage of oil through a broken ice field. With regard to vertical movement, Cox et al. (1980) postulate that oil/water interfacial tension partially controls the inception of the vertical migration in the brine drainage channels.

Aqueous Solubility

The values of aqueous solubility (solubility of oil in water) at 20°C for the No. 2 heating oil, Prudhoe Bay crude, and No. 4 fuel oil are also tabulated in Tables 2a through 2c. Plots of aqueous solubility vs. evaporative exposure for all three oils are shown in Figure 10. These plots show that the aqueous solubilities of all three oils decrease rapidly with evaporation from their initial values to negligible values within a week or so. In addition, the aqueous solubility appears to be quantitatively dependent on the evaporative exposure levels. The aqueous solubility affects the toxicity of the oil to marine life, particularly in the case of the Prudhoe Bay crude which has a high initial solubility (29.20 gm/m^3). The higher the solubility of the oil, the more damaging it may be to free-swimming marine organisms particularly in the juvenile stages. Thus for an oil spill on solid ice, it may be advisable to contain the oil on the ice for a period of time to minimize this damage.

Viscosity

Viscosity values at various temperatures (0°C, 10°C, 20°C, and 30°C) for No. 2 heating oil, Prudhoe Bay crude, and No. 4 fuel oil are tabulated in Tables 3a through 3c. Plots of viscosity at 20°C as measured at the R&D Center vs. evaporative exposure are given in Figures 11 through 13. Figure 11, the viscosity plot for No. 2 heating oil, shows little change in the oil viscosity (1 centipoise) with evaporation even after 10 days of exposure. The situation is completely different for Prudhoe Bay crude and No. 4 fuel oil which change significantly with evaporation. Even more important than evaporation is the effect of emulsification which required that emulsified samples be plotted separately. Figure 12a shows the effect of

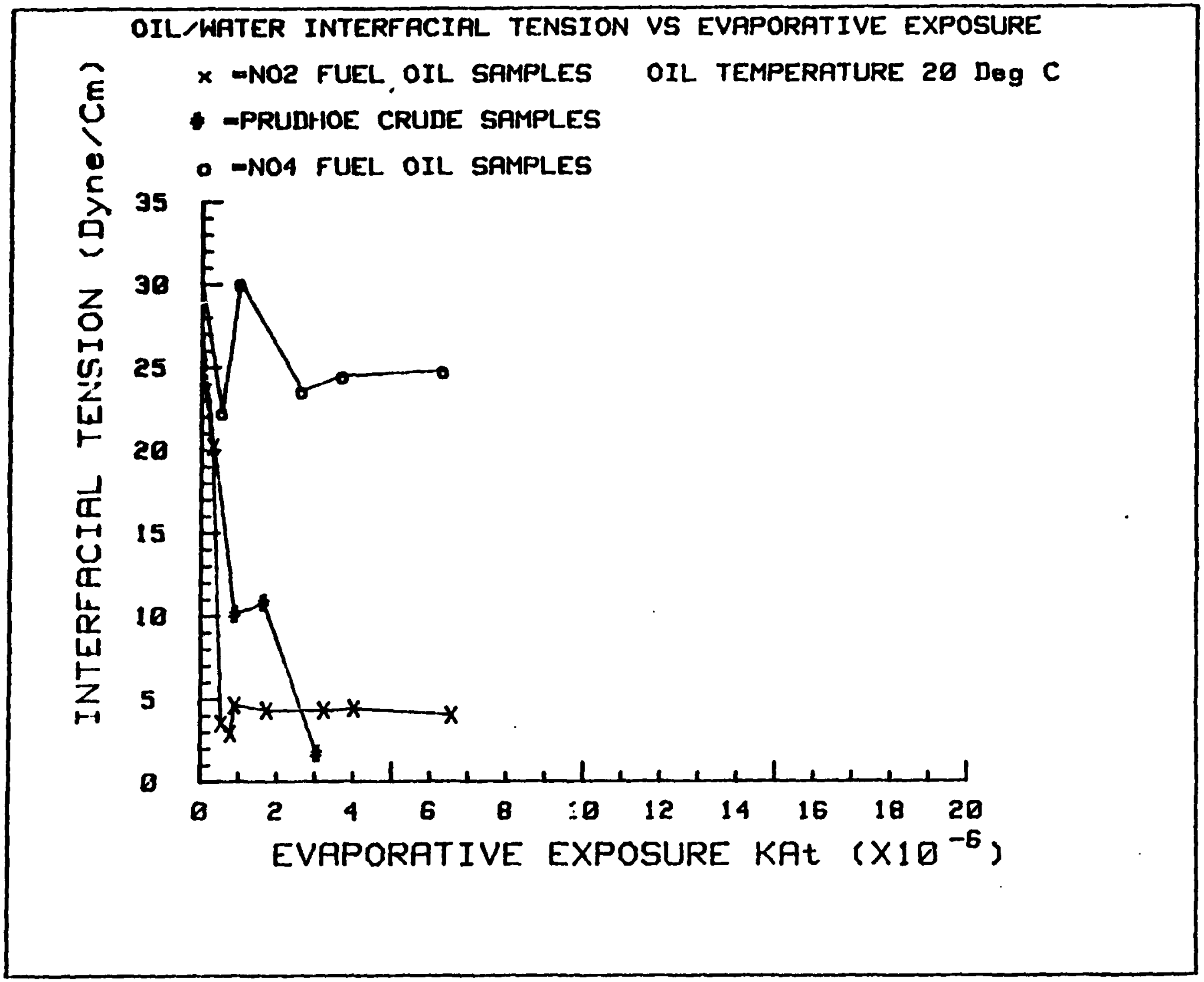

Figure 9 Oil/Water Interfacial Tension (at 20°C) vs. Evaporative Exposure for No.2 Heating Oil, Prudhoe Bay Crude Oil, and No. 4 Fuel Oil.

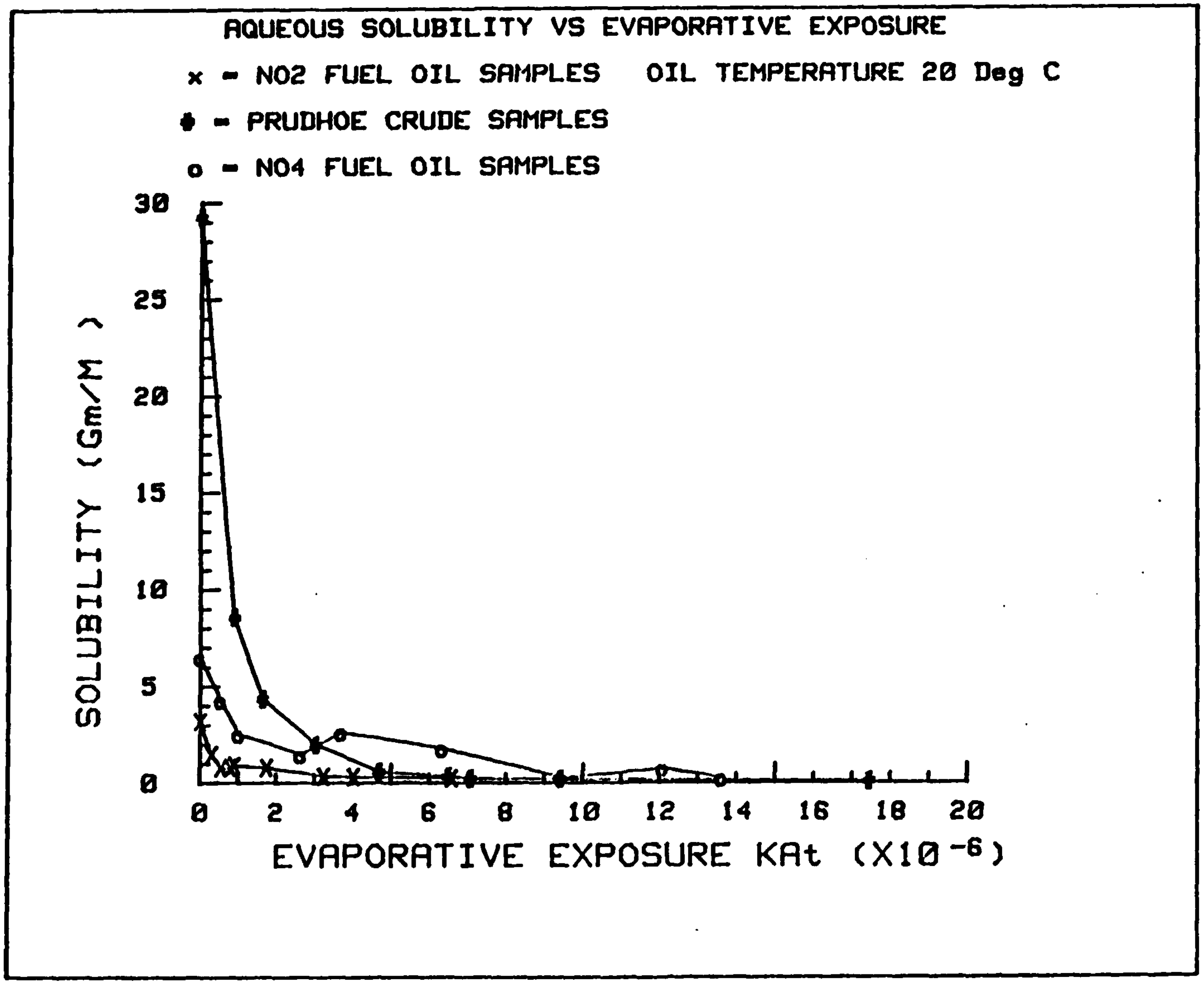

Figure 10 Aqueous Solubility (at 20° C) vs. Evaporative Exposure for No. 2 Heating Oil, Prudhoe Bay Crude Oil, and No. 4 Fuel Oil.

Table 3a Physical Properties (Viscosity, Pour Point, and Water Content) for No.2 Heating Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	VISCOSITY (CENTIPOISE) 0 DEG C	10 DEG C	20 DEG C	30 DEG C	R&DC	POUR POINT DEG C	OIL/WATER CONTENT (%OIL)
01	NO2 #01	.559	---	---	---	---	6.3	---	100.0
02	NO2 #02	1.021	---	---	---	---	---	---	---
03	NO2 #03	2.105	---	---	---	---	6.9	---	100.0
04	NO2 #04	3.582	---	---	---	---	6.8	---	100.0
05	NO2 #05	6.219	---	---	---	---	---	---	100.0
06	NO2 #06	0.000	---	---	---	---	---	---	---
07	NO2 #07	.278	---	---	---	---	6.5	---	100.0
08	NO2 #08	.547	9.6	---	4.9	---	---	-21.	100.0
09	NO2 #09	1.645	---	---	---	---	---	---	100.0
10	NO2 #10	2.730	---	---	---	---	---	---	100.0
11	NO2 #11	3.693	---	---	---	---	---	---	100.0
12	NO2 #12	5.450	---	---	---	---	---	---	100.0
13	NO2 #13	6.325	---	---	---	---	---	---	100.0
14	NO2 #14	9.090	---	---	---	---	---	---	78.5
15	NO2 #15	12.072	---	---	---	---	---	---	100.0
16	NO2 #16	.896	9.0	---	4.6	---	6.5	-21.	100.0
17	NO2 #17	2.631	---	---	---	---	---	---	98.5
18	NO2 #18	.200	---	---	---	---	---	---	100.0
19	NO2 #19	.305	8.3	---	4.3	---	5.9	-27.	100.0
20	NO2 #20	.787	8.9	---	4.7	---	6.1	-27.	100.0
21	NO2 #21	2.250	---	---	---	---	6.8	---	100.0
22	NO2 #22	3.633	---	---	---	---	---	---	100.0
23	NO2 #23	4.951	---	---	---	---	---	---	---
24	NO2 #24	5.366	---	---	---	---	---	---	100.0
25	NO2 #25	6.566	18.8	---	7.8	---	---	-19.	100.0
26	NO2 #26	13.584	---	---	---	---	---	---	100.0
27	NO2 #27	1.739	9.7	---	4.8	---	6.3	-21.	100.0
28	NO2 #28	3.235	11.3	---	5.6	---	6.8	-27.	100.0
29	NO2 #29	3.484	---	---	---	---	6.8	---	100.0
30	NO2 #30	4.016	12.6	---	5.9	---	6.9	-21.	100.0
31	NO2 ST1	0.000	---	---	---	---	5.9	---	100.0
32	NO2 ST2	0.000	7.7	---	4.0	---	6.1	-27.	100.0
33	NO2 ST3	0.000	---	---	---	---	---	---	100.0

Table 3b Physical Properties (Viscosity, Pour Point, and Water Content) for Prudhoe Bay Crude Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	VISCOSITY (CENTIPOISE) 0 DEG C	10 DEG C	20 DEG C	30 DEG C	R&DC	POUR POINT DEG C	OIL/WATER CONTENT (%OIL)
01	PBC #01	0.449	---	---	---	---	---	---	---
02	PBC #02	0.887	---	---	---	---	---	---	---
03	PBC #03	1.947	---	---	---	---	150.	---	100.0
04	PBC #04	3.188	---	---	---	---	217.	---	100.0
05	PBC #05	7.335	---	---	---	---	312.	---	72.5
06	PBC #06	13.071	---	---	---	---	457.	---	95.0
07	PBC #07	0.185	---	---	---	---	106.	---	100.0
08	PBC #08	0.707	---	---	---	---	242.	---	100.0
09	PBC #09	0.320	---	---	---	---	101.	---	100.0
10	PBC #10	1.068	---	---	---	---	---	---	95.0
11	PBC #11	1.134	---	---	---	---	---	---	100.0
12	PBC #12	1.645	---	1600.	200.	---	204.	---	100.0
13	PBC #13	2.730	---	---	---	---	204.	---	100.0
14	PBC #14	3.693	---	---	---	---	272.	---	100.0
15	PBC #15	5.450	---	---	---	---	354.	---	100.0
16	PBC #16	6.325	---	---	---	---	321.	---	100.0
17	PBC #17	9.090	---	---	---	---	---	---	100.0
18	PBC #18	12.072	---	---	---	---	692.	---	100.0
19	PBC #19	0.896	---	630.	130.	---	126.	6.0	100.0
20	PBC #20	2.631	---	---	---	---	524.	---	100.0
21	PBC #21	4.685	---	---	2400.	740.	3655.	12.0	77.5
22	PBC #22	6.494	---	---	6000.	2000.	8840.	15.0	90.0
23	PBC #23	7.189	---	---	---	---	4470.	---	75.0
24	PBC #24	9.418	---	---	10000.	4000.	10480.	15.0	96.0
25	PBC #25	10.926	---	---	---	---	10060.	---	100.0
26	PBC #26	1.011	---	---	---	---	152.	---	100.0
27	PBC #27	3.042	---	4000.	300.	---	---	9.0	100.0
28	PBC #28	4.250	---	---	---	---	314.	---	100.0
29	PBC #29	7.071	---	---	1000.	300.	1002.	12.0	100.0
30	PBC #30	8.829	---	---	---	---	---	---	100.0
31	PBC #31	6.895	---	---	---	---	683.	---	100.0
32	PBC #32	7.651	---	---	---	---	820.	---	100.0
33	PBC #33	9.713	---	---	---	---	1120.	---	100.0
34	PBC #34	13.605	---	---	---	---	6840.	---	98.5
35	PBC #35	17.443	---	---	9000.	4000.	11140.	18.0	95.0
36	PBC ST1	0.000	---	---	---	---	---	---	100.0
37	PBC ST2	0.000	1500.	96.	35.	---	---	-2.0	100.0
38	PBC ST3	0.000	---	---	---	---	---	---	100.0

Table 3c Physical Properties (Viscosity, Pour Point, and Water Content) for No.4 Fuel Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	VISCOSITY (CENTIPOISE) 0 DEG C	10 DEG C	20 DEG C	30 DEG C	R&DC	POUR POINT DEG C	OIL/WATER CONTENT (%OIL)
01	NO4 #01	0.645	---	---	---	---	110.	---	100.0
02	NO4 #02	0.906	---	---	---	---	---	---	100.0
03	NO4 #03	1.579	---	---	---	---	147.	---	100.0
04	NO4 #04	2.677	---	---	---	---	228.	---	100.0
05	NO4 #05	0.784	---	---	---	---	82.	---	100.0
06	NO4 #06	1.493	---	---	---	---	266.	---	100.0
07	NO4 #07	0.547	---	70.	30.	---	75.	0.0	100.0
08	NO4 #08	1.645	---	---	---	---	63.	---	100.0
09	NO4 #09	2.730	---	---	---	---	42.	---	100.0
10	NO4 #10	3.693	---	---	106.	68.	75.	9.0	100.0
11	NO4 #11	5.450	---	---	---	---	129.	---	100.0
12	NO4 #12	6.325	---	---	194.	86	630.	12.0	100.0
13	NO4 #13	9.090	---	---	---	---	288.	---	100.0
14	NO4 #14	12.072	---	---	---	---	730.	18.0	100.0
15	NO4 #15	0.896	---	---	---	---	32.	---	100.0
16	NO4 #16	2.631	---	360.	79.	---	360.	6.0	100.0
17	NO4 #17	4.685	---	---	---	---	7940.	---	100.0
18	NO4 #18	6.494	---	---	---	---	3600.	---	100.0
19	NO4 #19	7.189	---	---	---	---	10200.	---0	97.5
20	NO4 #20	9.418	---	---	---	---	26700.	46.0	100.0
21	NO4 #21	10.926	---	---	---	---	26000.	---	100.0
22	NO4 #22	1.011	---	167.	---	---	42.	3.0	100.0
23	NO4 #23	3.042	---	---	---	---	53.	---	100.0
24	NO4 #24	4.250	---	---	---	---	285.	---	100.0
25	NO4 #25	7.071	---	---	---	---	9440.	---	99.5
26	NO4 #26	8.829	---	---	---	---	5230.	---	100.0
27	NO4 #27	6.892	---	---	---	---	2288.	---	97.0
28	NO4 #28	7.651	---	---	---	---	1660.	---	100.0
29	NO4 #29	9.713	---	---	---	---	4710.	---	95.0
30	NO4 #30	13.605	---	---	---	4000.	7780.	24.0	99.0
31	NO4 #31	17.443	---	---	---	---	9880.	---	100.0
32	NO4 ST1	0.000	---	---	---	---	24.	---	100.0
33	NO4 ST2	0.000	---	47.	23.	---	24.	-3.0	100.0
34	NO4 ST3	0.000	---	---	---	---	24.	---	100.0

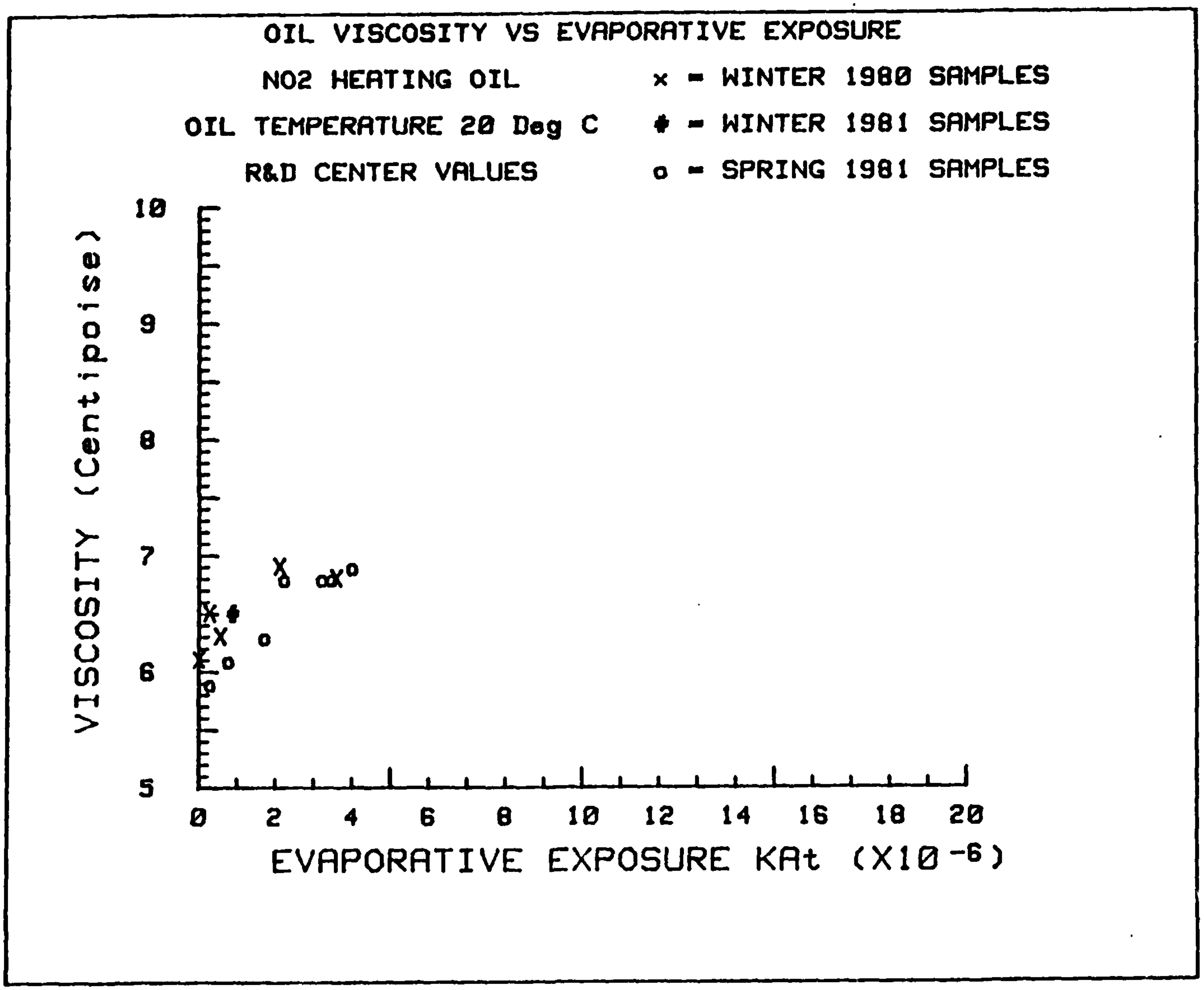

Figure 11 Viscosity (at 20^0 C) vs. Evaporative Exposure for No. 2 Heating Oil.

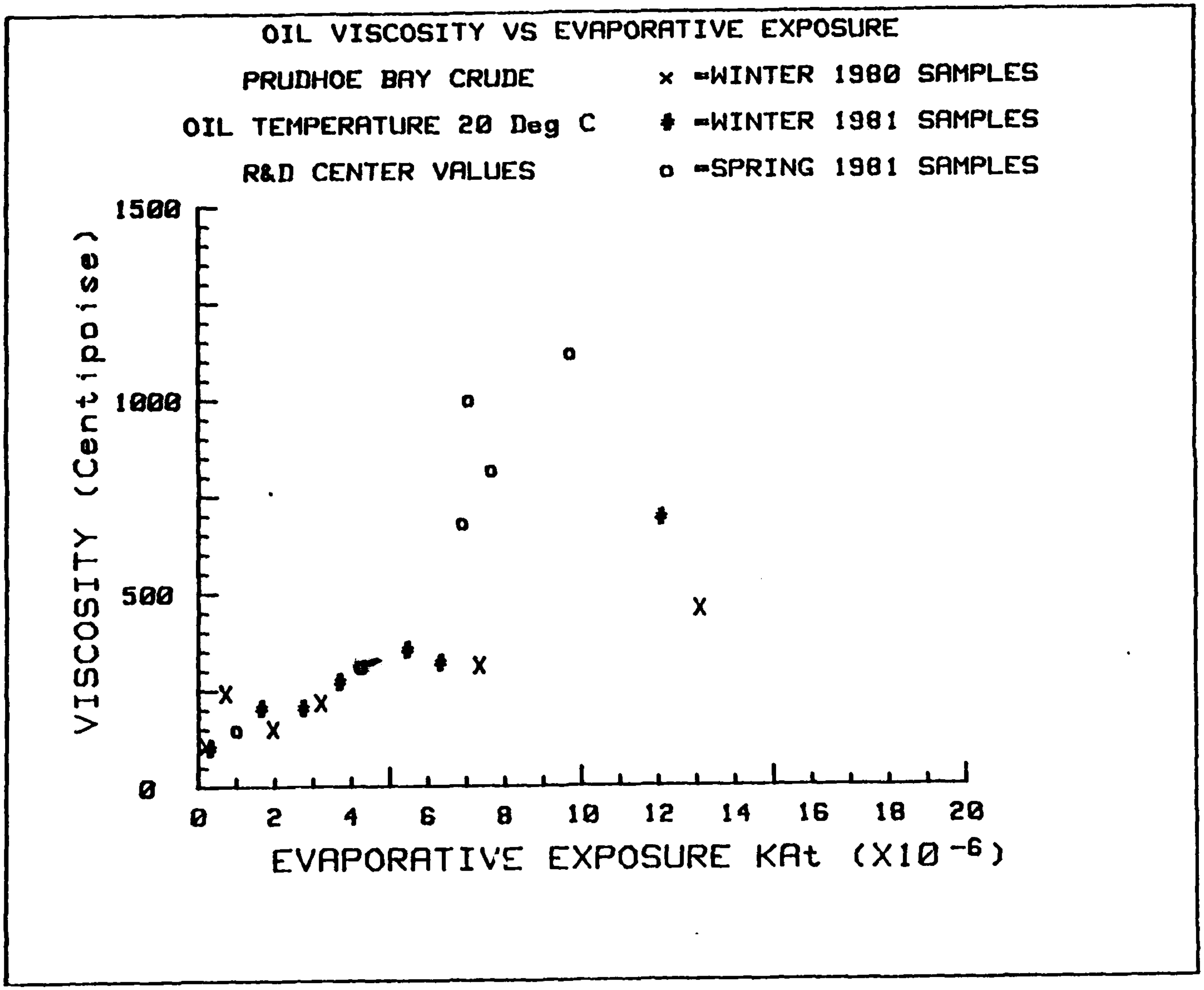

Figure 12a Viscosity (at 20^0 C) vs. Evaporative Exposure for Prudhoe Bay Crude Oil (Emulsified Samples Not Included).

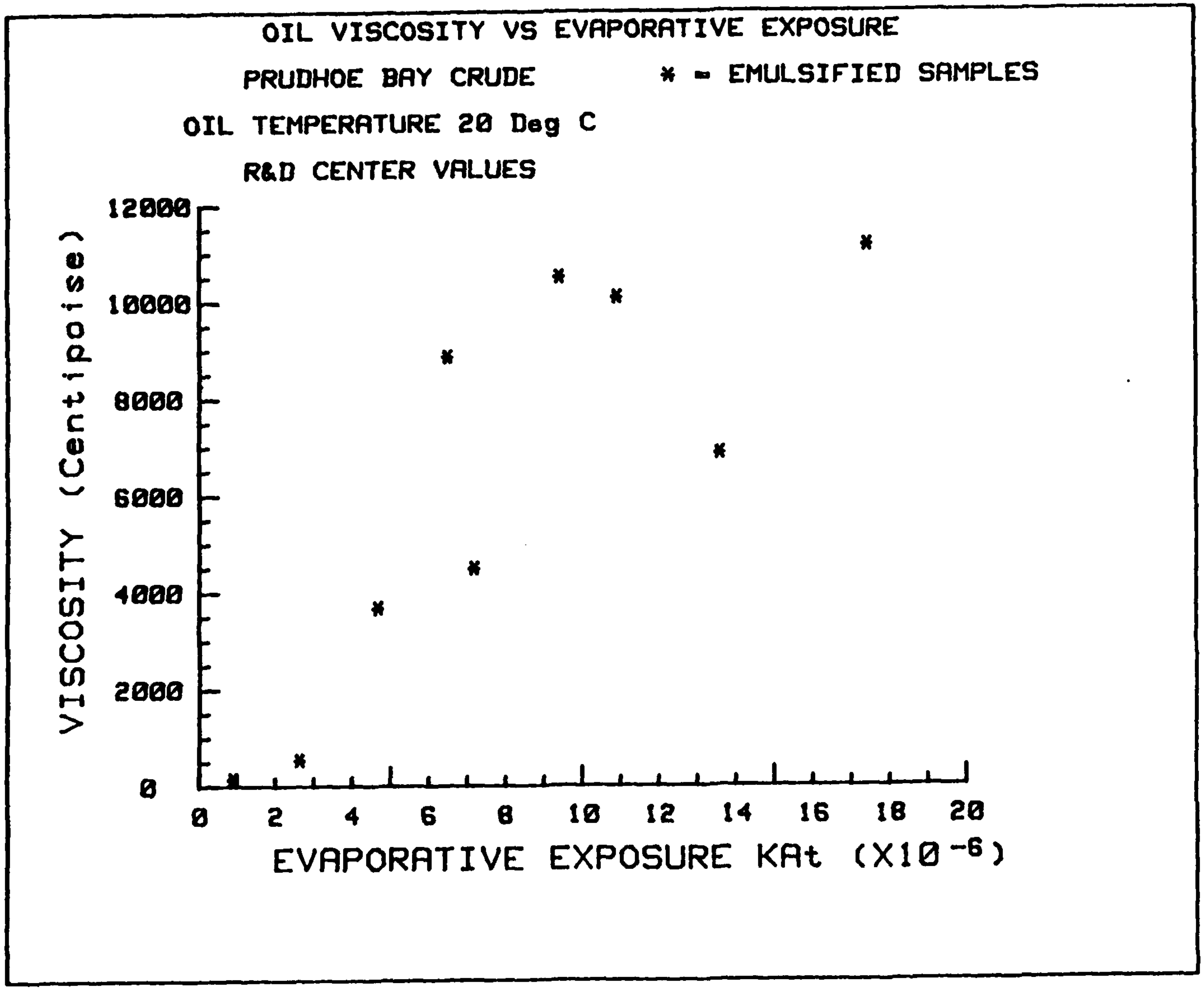

Figure 12b Viscosity (at 20^0 C) vs. Evaporative Exposure for Emulsified Prudhoe Bay Crude Oil Samples.

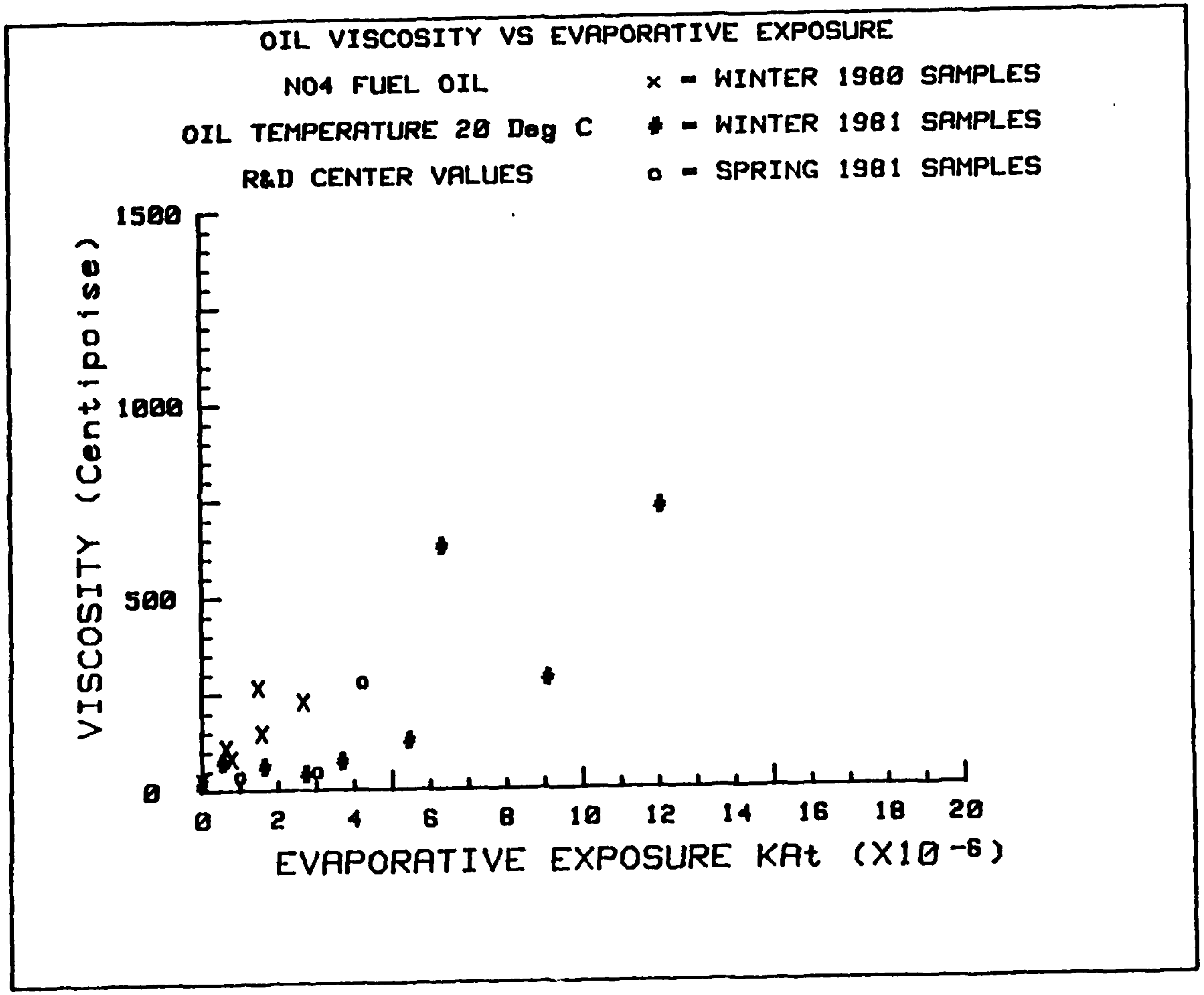

Figure 13a Viscosity (at 20° C) vs. Evaporative Exposure for No. 4 Fuel Oil (Emulsified Samples Not Included).

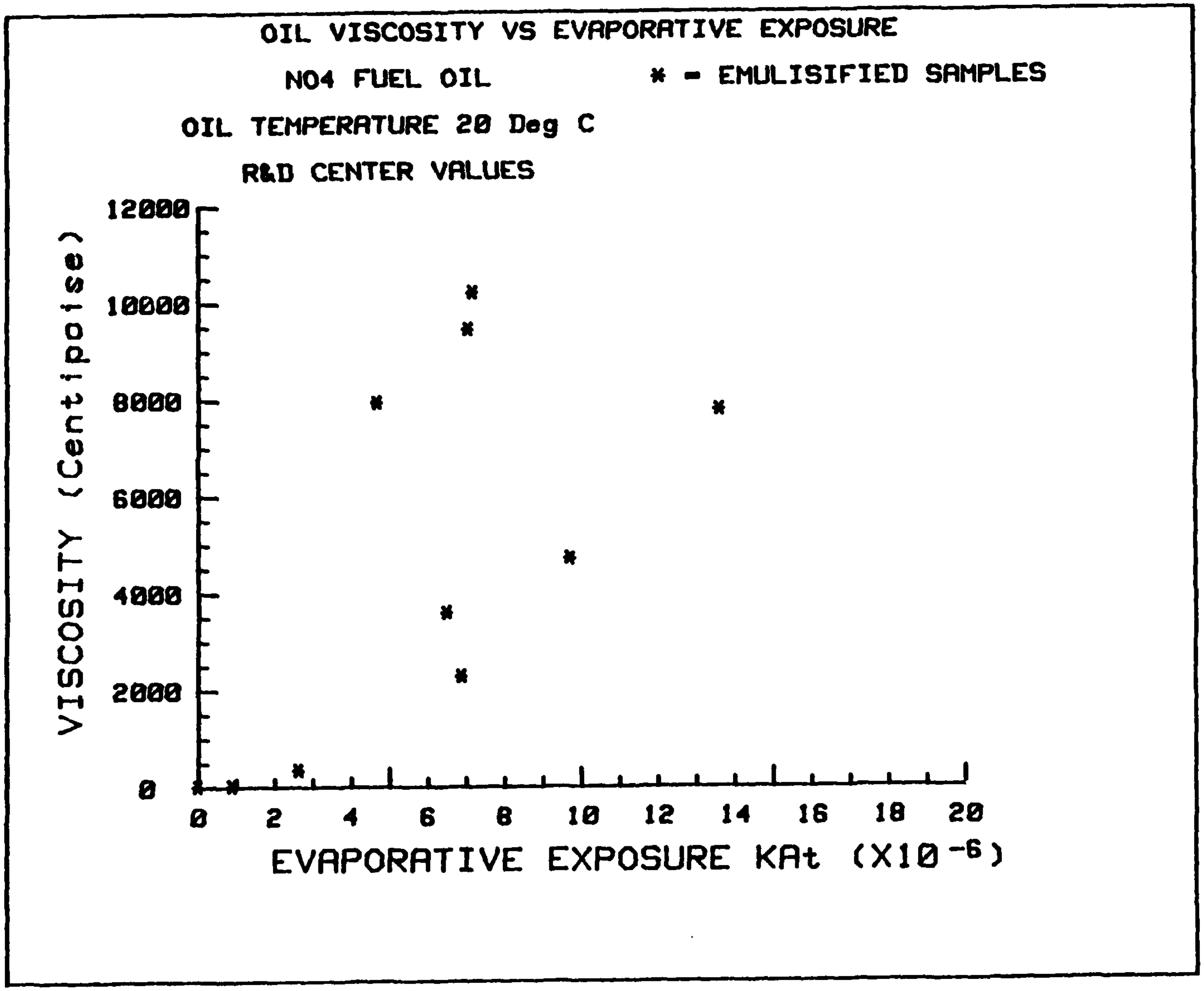

Figure 13b Viscosity (at 20° C) vs. Evaporative Exposure for Emulsified No. 4 Fuel Oil Samples.

evaporative exposure on the viscosity of Prudhoe Bay Crude with the viscosity increasing from an initial value of about 100 cp to over 500 cp (sample 18) after a month's exposure. Some of the samples weathered during warmer temperatures (Spring 1931) have viscosities over 1000 cp; however, here some emulsification is suspected for these high values. The significant impact of emulsification on viscosity for Prudhoe Bay crude is clearly shown in Figure 12b. Here viscosity values of over 10,000 cp are attained, with no discernible dependence on evaporative exposure. The results are much the same for the No. 4 fuel oil as shown in Figures 13a and 13b. Thus, the change in viscosity with both evaporation and emulsification appears to be restricted to the heavier oils. Unfortunately, the sensitivity of oil viscosity to emulsification will make the modelling of this parameter as a function of evaporative exposure difficult.

This change in viscosity with both evaporation and emulsification has important implications on the behavior and cleanup of an Arctic oil spill, where viscosities will be further increased by colder temperatures. Various researchers (Uzuner et al., 1978, Cox et al., 1980, and Free et al., 1981) have shown that the horizontal spreading rate on ice, under ice, and in a broken ice field is largely controlled by the viscosity of the oil, with higher viscosities retarding spill movement. Likewise, Cox et al. (1980) have postulated that the vertical migration rate of oil up through the brine drainage channels is also dependent on the viscosity. With regard to cleanup of the spill, the viscosity of the oil may dictate the equipment used to recover the oil in that high viscosities may substantially reduce the effectiveness of suction hoses and skimmers. Likewise, higher viscosities may limit the usefulness of dispersants which require turbulent mixing with the oil to be effective.

Pour Point

Closely related to the viscosity of the oil is the pour point, which is that temperature at which the oil congeals and no longer flows freely. Pour point values for No. 2 heating oil, Prudhoe Bay crude, and No. 4 fuel oil are given in Tables 3a through 3c. Plots of pour point vs. evaporative exposure for all three types of oil are given in Figure 14. Figure 14 shows that pour point generally increases with evaporative exposure. The pour point of No. 2 heating oil increases from an initial value of -27°C to a final value of -19°C after 3 weeks of exposure. The increase is somewhat greater for Prudhoe Bay crude (from -2°C to 18°C) and No. 4 fuel oil (from -3°C to 24°C) after a month of exposure. A pour point value of 46°C was recorded for No. 4 fuel oil sample number 20; however, this value appears to be anomalous. It is important to note that unlike oil viscosity, the pour point is relatively insensitive to emulsification. This probably applies for all pour points above the freezing temperature of water (0°C). Likewise, there appears to be a well-defined quantitative dependence of pour point on evaporative exposure, which makes the modelling of pour point as a function of evaporative exposure feasible.

The implications of the increase in pour point on the behavior and cleanup of the oil are the same as for the increase in viscosity. It is also important to recognize that all of the theoretical models for the physical behavior of an oil spill (i.e., spreading rate, final thickness, vertical migration rate, dispersion rate, etc.) assume the applicability of various

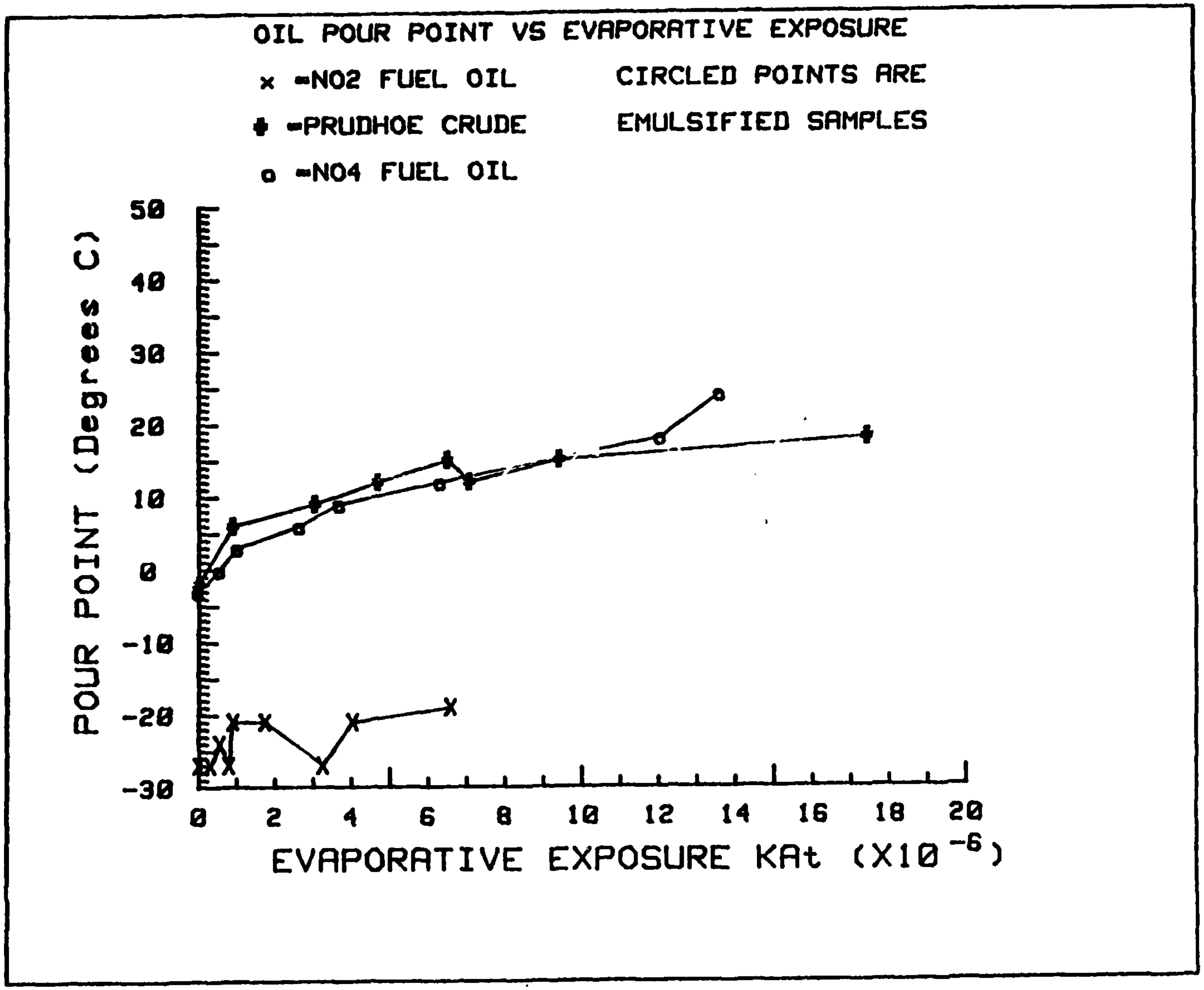

Figure 14 Pour Point vs. Evaporative Exposure for No. 2 Heating Oil, Prudhoe Bay Crude Oil, and No. 4 Fuel Oil.

fluid dynamic principles. However, the pour point represents that temperature at which the oil behaves more like a semi-solid than a fluid. Therefore, when attempting to model an oil spill where the oil temperature is at or near the pour point temperature (which changes with evaporation), a great deal of inaccuracy in model predictions can be expected.

Water Content

Values of the fraction of oil vs. water in the sample (expressed as % oil vs. water) were obtained for all three oils using the technique outlined in Appendix B. These values are listed in Tables 3a through 3c. This analysis was performed as a cursory check for emulsification to aid in the grouping of the samples, and no quantitative interpretation of the results was attempted.

6.3 Gas Chromatograph Analysis

In addition to the physical properties analysis, a Gas Chromatography (GC) analysis was conducted by the R&D Center Chemistry Branch to study the changes in the chemical composition of the oil samples with weathering. The equipment and procedures for this analysis are outlined in Appendix B. GC data processing consisted of measuring the heights of the various hydrocarbon peaks on the graphic output (C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}) and computing ratios with respect to the C_{20} peak height (i.e., C_{10}/C_{20}, C_{12}/C_{20}, C_{14}/C_{20}, C_{16}/C_{20}, C_{18}/C_{20}). This normalization procedure will allow comparison of the results of this study with GC scans run by other researchers. The values of the GC ratios for No. 2 heating oil, Prudhoe Bay crude, and No. 4 fuel oil are given in Tables 4a through 4c. The values of C_{12}/C_{20}, C_{14}/C_{20}, C_{16}/C_{20}, and C_{18}/C_{20} vs. evaporative exposure for the various oil types and sample groupings are plotted in Figures 15a-c, 16a-d, and 17

The primary objective of this analysis was to check the correlation of the GC ratios with "evaporative exposure." Flanigan and Bentz (1977) have suggested that GC data on the C_{12} or C_{14} peaks could provide rough estimates of the weathering time. Therefore, it seemed possible that C_{12} and C_{14} data could also provide estimates of evaporative exposure, which in turn would provide insight into the physical properties of the oil as discussed in the previous section. This could lead to a valuable technique whereby an oil sample from a spill of undetermined origin could be analyzed, perhaps on a field GC unit, to give the C_{12}/C_{20} and C_{14}/C_{20} values. The C_{12}/C_{20} and C_{14}/C_{20} values would then be used to estimate the evaporative exposure. This evaporative exposure estimate could in turn be used to predict the physical properties and combustibility of the oil which would aid the on-scene coordination in planning an effective cleanup strategy.

Figures 15a through 15c show the GC ratio plots for the Winter 1980, Winter 1981, and Spring 1981 groups of the No. 2 heating oil samples. The C_{10}/C_{20} ratios have been omitted from the plots as the C_{10} hydrocarbons generally disappear within 24 hours. The C_{12}/C_{20} ratios for all three groups show a well-defined decrease with evaporative exposure over periods of up to 3 weeks (e.g., Samples 8-14, Winter 1981 group). The C_{14}/C_{20} ratios from No. 2 oil show considerably less change except perhaps for the Spring 1981 group. As expected, the C_{16}/C_{20}, and C_{18}/C_{20} ratios show almost

Table 4a Gas Chromatograph Data for No.2 Heating Oil.

#	SAMPLE	EVAP EXPOSURE x 10^{-6}	C10/C20	C12/C20	C14/C20	C16/C20	C18/C20
01	NO2 #01	.559	.25	1.52	2.33	2.50	1.69
02	NO2 #02	1.021	0.00	1.26	2.35	2.61	1.74
03	NO2 #03	2.105	0.00	1.24	2.38	2.56	1.69
04	NO2 #04	3.582	0.00	1.02	2.35	2.57	1.71
05	NO2 #05	6.219	0.00	.69	2.25	2.56	1.73
06	NO2 #06	0.000	0.00	0.00	1.75	2.37	1.62
07	NO2 #07	.278	.25	1.53	2.33	2.28	1.63
08	NO2 #08	.547	0.00	1.42	2.23	2.13	1.47
09	NO2 #09	1.645	0.00	1.02	2.27	2.15	1.52
10	NO2 #10	2.730	0.00	.87	2.30	2.20	1.53
11	NO2 #11	3.693	0.00	.72	2.17	2.32	1.62
12	NO2 #12	5.450	0.00	.61	2.18	2.24	1.56
13	NO2 #13	6.325	0.00	.43	2.08	2.13	1.51
14	NO2 #14	9.090	0.00	.33	2.11	2.17	1.51
15	NO2 #15	12.072	——	——	——	——	——
16	NO2 #16	.896	0.00	1.41	2.44	2.28	1.58
17	NO2 #17	2.631	0.00	.48	2.18	2.21	1.54
18	NO2 #18	.200	0.00	1.61	2.40	2.20	1.51
19	NO2 #19	.305	0.00	1.27	2.40	2.36	1.62
20	NO2 #20	.787	0.00	1.31	2.44	2.28	1.59
21	NO2 #21	2.250	0.00	1.04	2.29	2.18	1.50
22	NO2 #22	3.633	0.00	.34	2.24	2.17	1.51
23	NO2 #23	4.951	0.00	.49	1.89	2.44	1.59
24	NO2 #24	5.366	0.00	.18	2.15	2.16	1.50
25	NO2 #25	6.566	0.00	0.00	.32	1.73	1.46
26	NO2 #26	13.584	0.00	0.00	.78	0.00	1.47
27	NO2 #27	1.739	0.00	1.35	2.38	2.20	1.53
28	NO2 #28	3.235	0.00	1.07	2.29	2.16	1.51
29	NO2 #29	3.484	0.00	.87	2.34	2.22	1.54
30	NO2 #30	4.016	0.00	.55	2.26	2.17	1.52
31	NO2 ST1	0.000	.53	1.49	2.36	2.55	1.68
32	NO2 ST2	0.000	.41	1.73	2.37	2.23	1.53
33	NO2 ST3	0.000	0.00	1.53	2.47	2.27	1.58

Table 4b Gas Chromatograph Data for Prudhoe Bay Crude Oil.

#	SAMPLE	EVAP EXPOSURE $\times 10^{-6}$	C10/C20	C12/C20	C14/C20	C16/C20	C18/C20
01	PBC #01	.449	.99	1.59	1.57	1.48	1.15
02	PBC #02	.887	.79	1.46	1.54	1.45	1.12
03	PBC #03	1.947	.60	1.36	1.53	1.51	1.13
04	PBC #04	3.188	.30	1.13	1.51	1.43	1.12
05	PBC #05	7.335	.10	.78	1.45	1.41	1.10
06	PBC #06	13.071	0.00	.30	1.38	1.40	1.12
07	PBC #07	.185	1.00	1.57	1.60	1.42	1.12
08	PBC #08	.707	.34	1.32	1.61	1.49	1.18
09	PBC #09	.320	0.00	1.51	1.58	1.45	1.13
10	PBC #10	1.068	0.00	1.11	1.53	1.47	1.15
11	PBC #11	1.134	0.00	1.31	1.54	1.48	1.13
12	PBC #12	1.645	0.00	1.25	1.52	1.44	1.12
13	PBC #13	2.730	0.00	1.11	1.52	1.45	1.11
14	PBC #14	3.693	0.00	1.10	1.50	1.43	1.11
15	PBC #15	5.450	0.00	.70	1.48	1.45	1.14
16	PBC #16	6.325	0.00	.77	1.45	1.42	1.10
17	PBC #17	9.090	0.00	.37	1.22	1.35	1.12
18	PBC #18	12.072	0.00	.32	1.29	1.44	1.14
19	PBC #19	.896	0.00	1.41	1.55	1.43	1.11
20	PBC #20	2.631	0.00	.39	1.37	1.43	1.13
21	PBC #21	4.685	0.00	.32	1.11	1.21	1.08
22	PBC #22	6.494	0.00	.17	1.05	1.32	1.10
23	PBC #23	7.189	0.00	.13	.98	1.26	1.11
24	PBC #24	9.418	0.00	.05	.79	1.23	1.08
25	PBC #25	10.926	0.00	.03	.67	1.21	1.09
26	PBC #26	1.011	0.00	1.31	1.51	1.43	1.12
27	PBC #27	3.042	0.00	.98	1.49	1.45	1.12
28	PBC #28	4.250	0.00	.39	1.46	1.42	1.11
29	PBC #29	7.071	0.00	.17	1.19	1.39	1.13
30	PBC #30	8.829	0.00	.07	1.05	1.38	1.11
31	PBC #31	6.895	0.00	.19	1.31	1.42	1.11
32	PBC #32	7.651	0.00	.07	1.21	1.26	1.10
33	PBC #33	9.713	0.00	0.00	.92	1.37	1.10
34	PBC #34	13.605	0.00	0.00	.44	1.27	1.12
35	PBC #35	17.443	.14	1.07	1.10	1.00	1.00
36	PBC ST1	0.000	1.05	1.30	1.30	1.24	1.05
37	PBC ST2	0.000	1.57	1.51	1.51	1.44	1.16
38	PBC ST3	0.000	0.00	1.56	1.55	1.46	1.13

Table 4c Gas Chromatograph Data for No.4 Fuel Oil.

#	SAMPLE	EVAP EXPOSURE x 10^{-6}	C10/C20	C12/C20	C14/C20	C16/C20	C18/C20
01	NO4 #01	.645	0.00	.74	1.70	1.52	1.22
02	NO4 #02	.906	0.00	.67	1.58	1.50	1.25
03	NO4 #03	1.579	0.00	.71	1.75	1.63	1.17
04	NO4 #04	2.677	0.00	.63	1.67	1.58	1.17
05	NO4 #05	.784	.72	2.28	2.68	1.80	1.12
06	NO4 #06	1.493	.20	2.08	2.76	1.88	1.12
07	NO4 #07	.547	0.00	3.59	3.38	1.95	1.08
08	NO4 #08	1.645	0.00	2.10	2.80	1.90	1.05
09	NO4 #09	2.730	0.00	2.26	2.47	1.79	.95
10	NO4 #10	3.673	0.00	1.37	2.61	1.95	1.05
11	NO4 #11	5.450	0.00	1.77	2.45	1.77	.98
12	NO4 #12	6.325	0.00	1.00	2.18	1.73	.76
13	NO4 #13	9.090	0.00	1.04	2.00	1.31	.96
14	NO4 #14	12.072	0.00	.16	1.79	1.42	.95
15	NO4 #15	.896	0.00	2.26	2.42	1.68	1.00
16	NO4 #16	2.631	0.00	1.67	2.29	1.48	1.00
17	NO4 #17	4.685	0.00	0.00	2.00	1.33	1.11
18	NO4 #18	6.494	0.00	0.00	1.67	1.25	.72
19	NO4 #19	7.189	0.00	0.00	1.76	1.35	1.00
20	NO4 #20	9.418	0.00	0.00	1.13	1.25	1.00
21	NO4 #21	10.926	0.00	0.00	1.07	1.33	1.07
22	NO4 #22	1.011	0.00	2.14	2.48	1.83	.75
23	NO4 #23	3.042	0.00	2.05	2.71	1.93	1.07
24	NO4 #24	4.256	0.00	1.14	2.52	1.91	1.09
25	NO4 #25	7.071	0.00	0.00	1.95	1.55	1.00
26	NO4 #26	8.829	0.00	0.00	1.74	1.56	.96
27	NO4 #27	6.895	0.00	0.00	1.75	1.30	.85
28	NO4 #28	7.651	0.00	0.00	1.93	1.60	.73
29	NO4 #29	9.713	0.00	0.00	1.61	1.54	.93
30	NO4 #30	13.605	----	----	----	----	----
31	NO4 #31	17.443	----	----	----	----	----
32	NO4 ST1	0.000	0.00	.96	1.70	1.65	1.17
33	NO4 ST2	0.000	0.00	3.28	2.77	1.85	1.00
34	NO4 ST3	0.000	0.00	3.20	2.70	1.83	.78

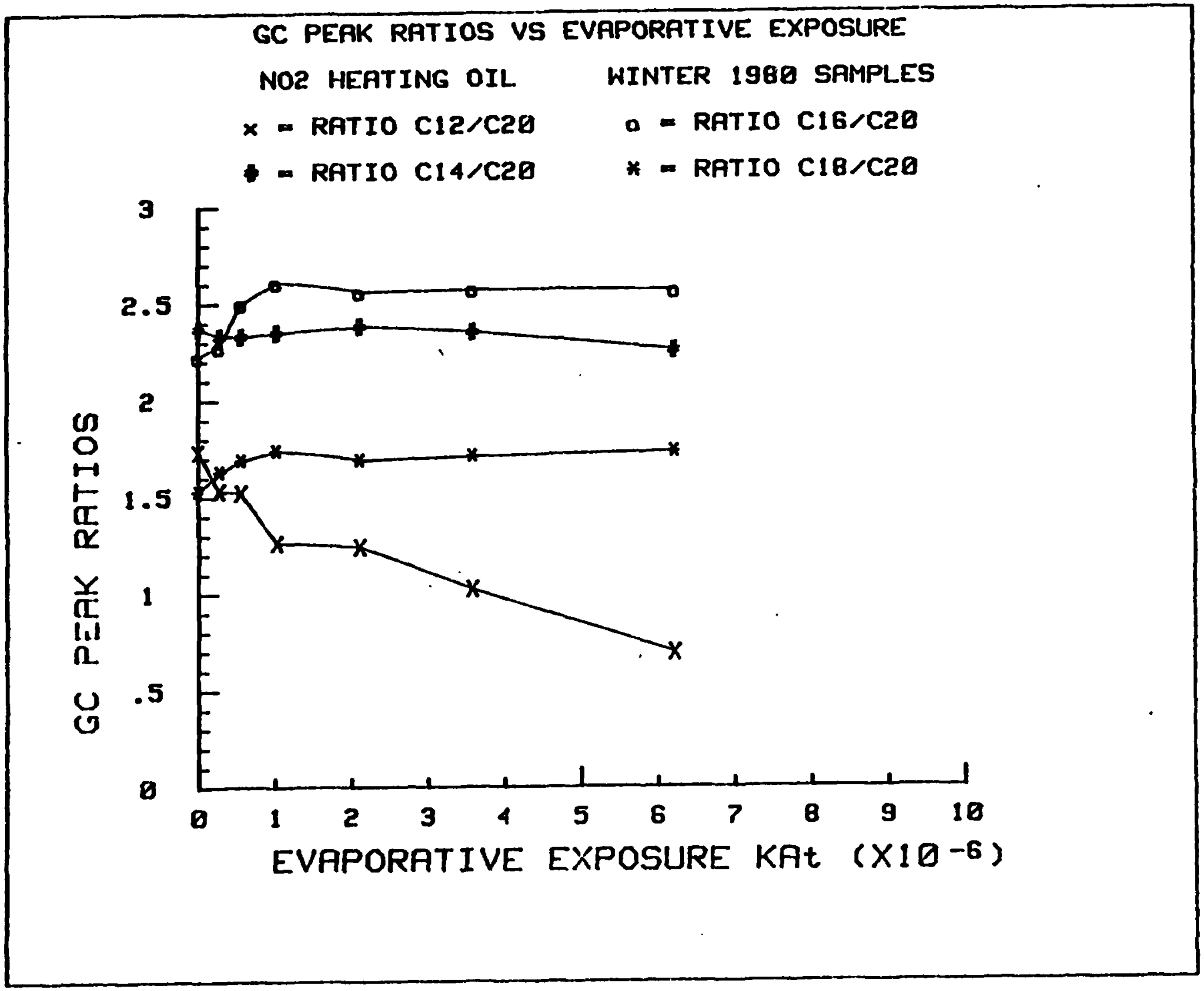

Figure 15a GC Peak Ratios vs. Evaporative Exposure for Winter 1980 Group, No. 2 Heating Oil.

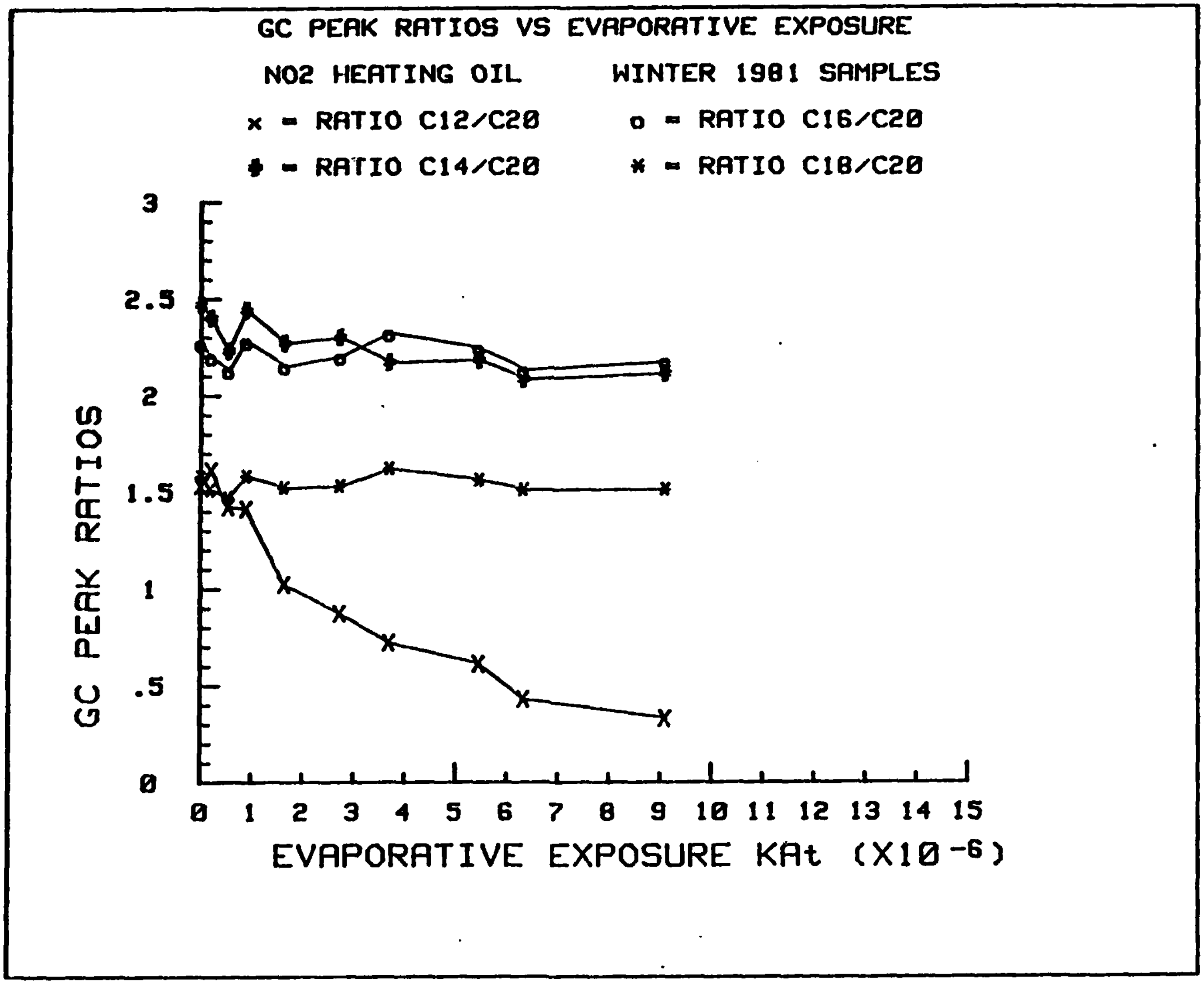

Figure 15b GC Peak Ratios vs. Evaporative Exposure for Winter 1981 Group, No. 2 Heating Oil.

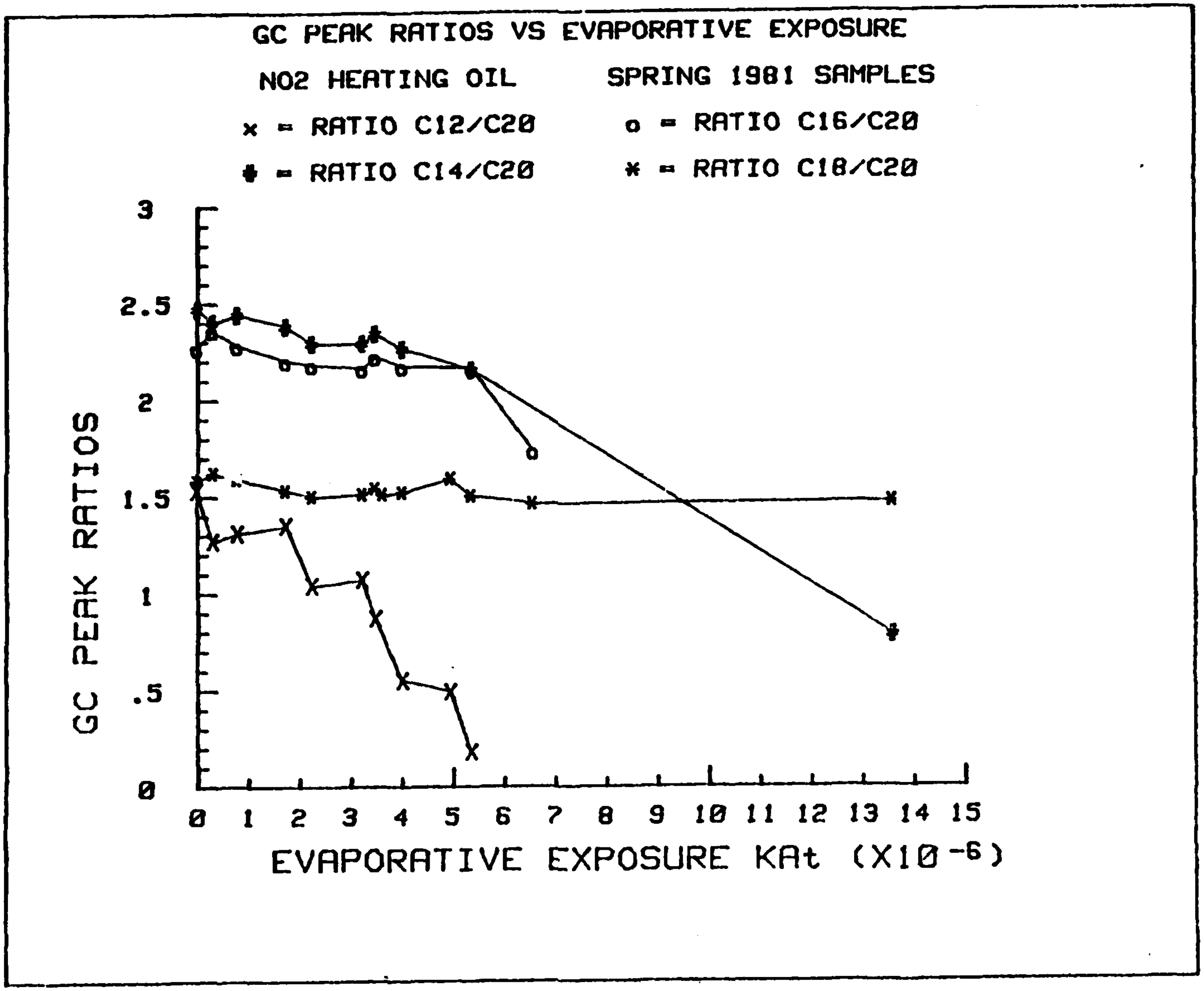

Figure 15c GC Peak Ratios vs. Evaporative Exposure for Spring 1981 Group, No. 2 Heating Oil.

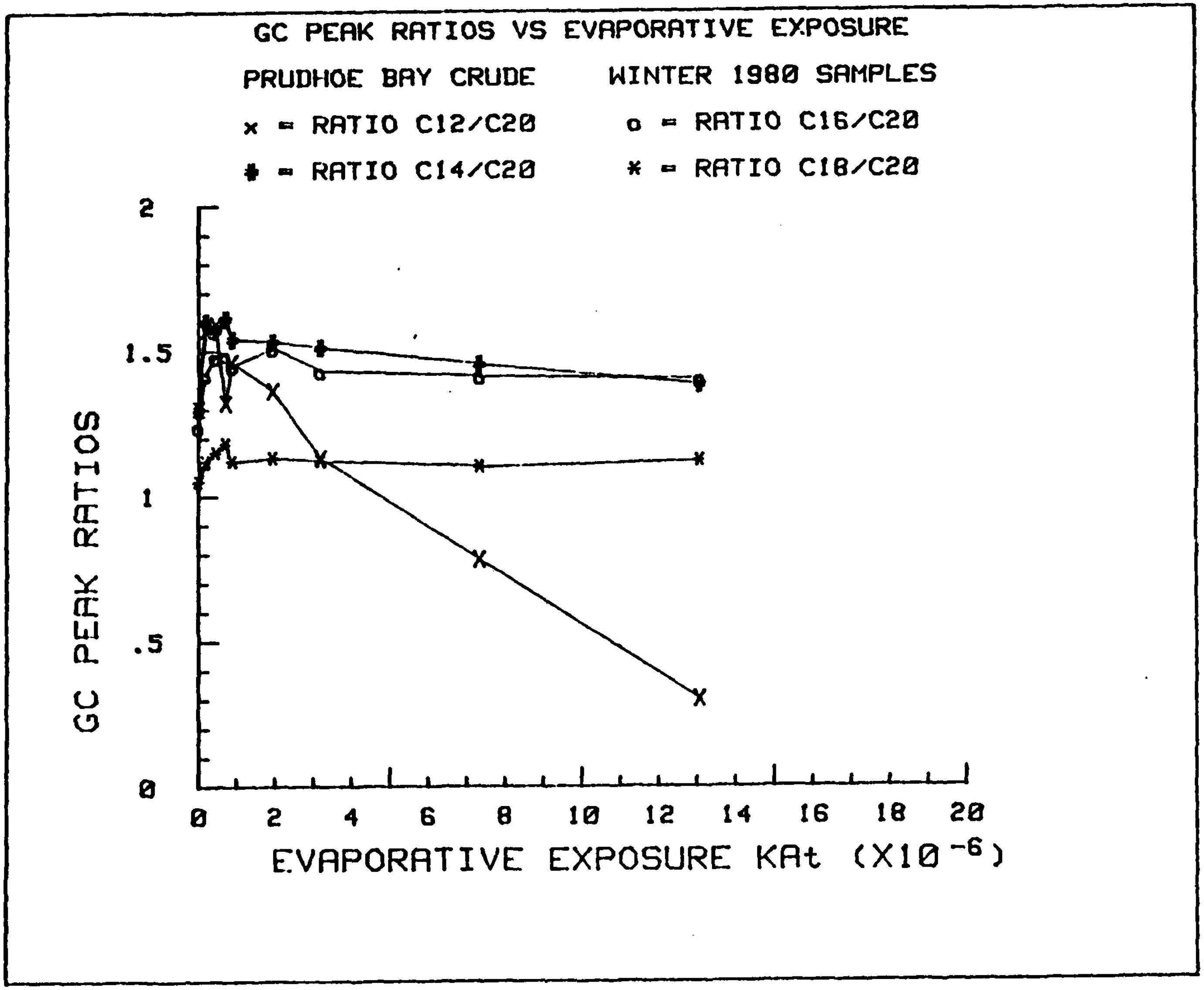

Figure 16a GC Peak Ratios vs. Evaporative Exposure for Winter 1980 Group, Prudhoe Bay Crude Oil.

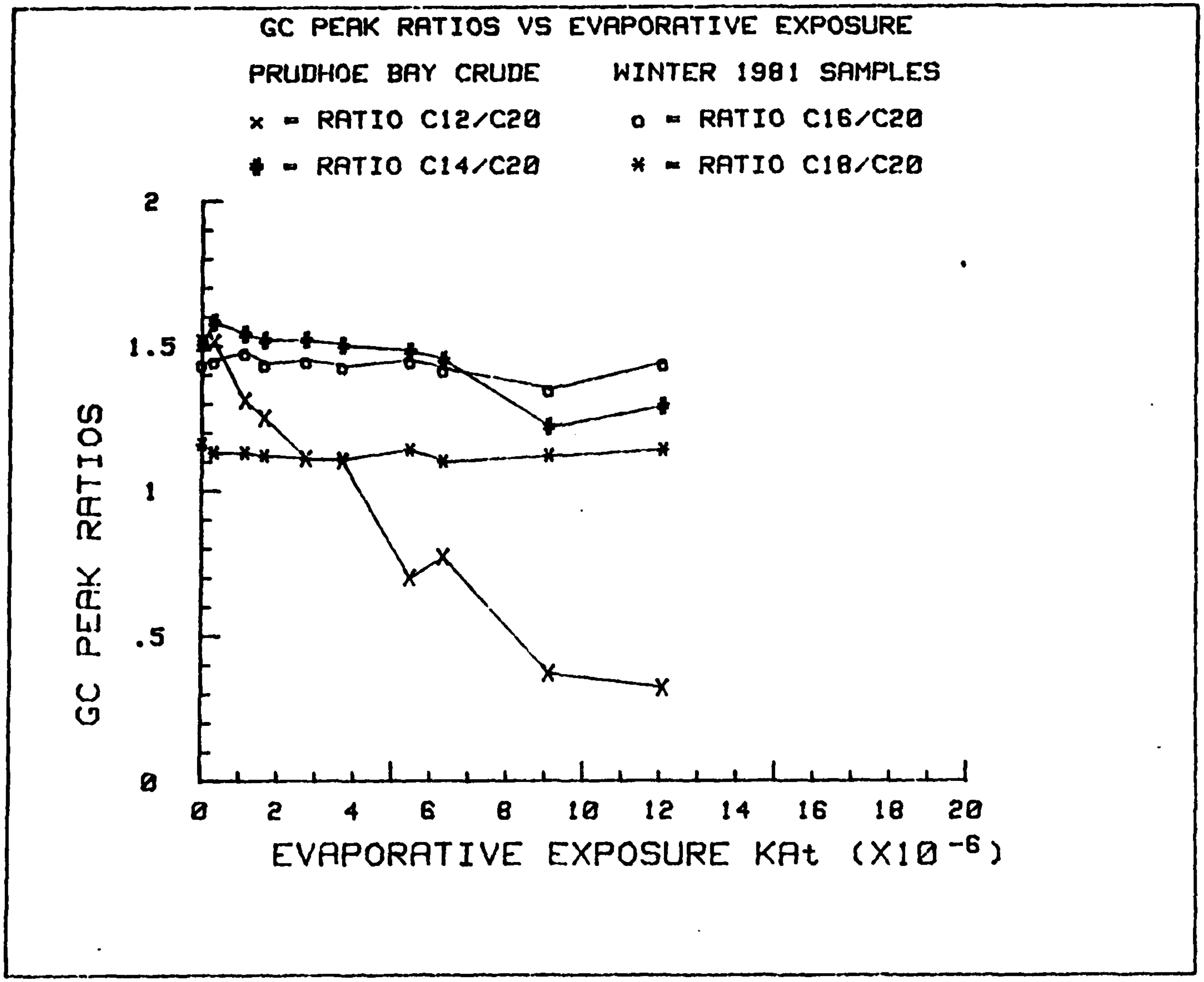

Figure 16b GC Peak Ratios vs. Evaporative Exposure for Winter 1981 Group, Prudhoe Bay Crude Oil.

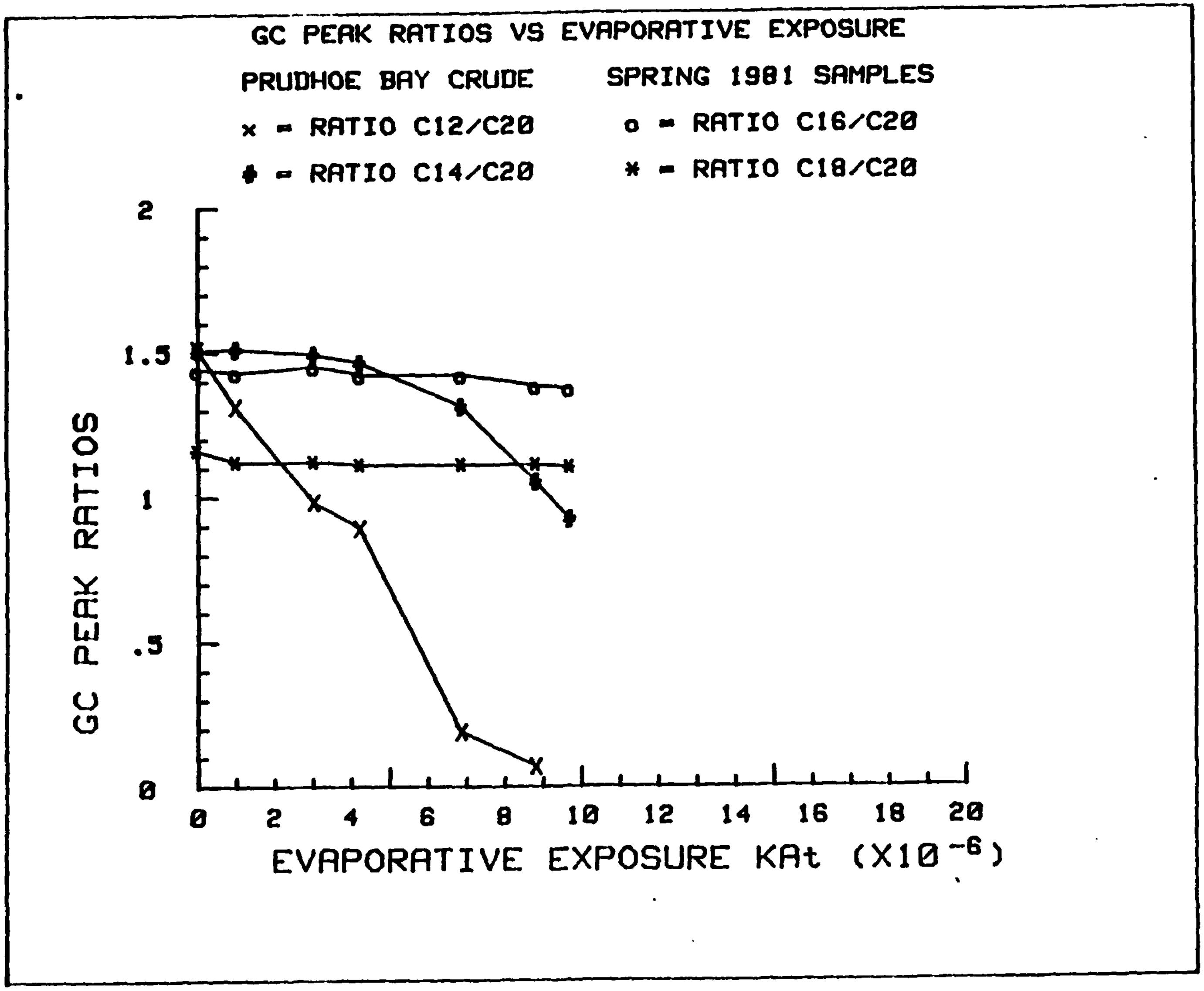

Figure 16c GC Peak Ratios vs. Evaporative Exposure for Spring 1981 Group, Prudhoe Bay Crude Oil.

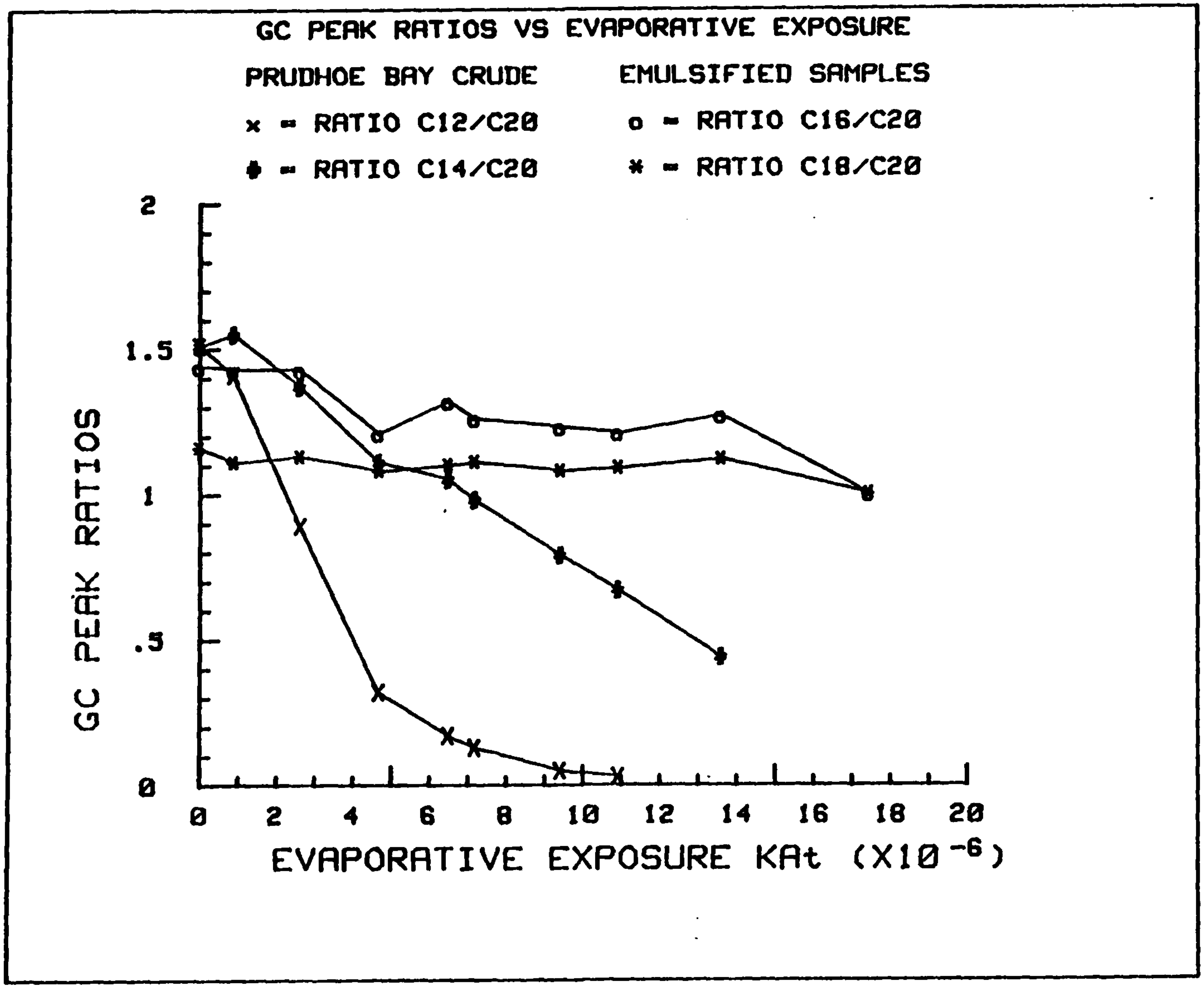

Figure 16d GC Peak Ratios vs. Evaporative Exposure for Emulsified Group, Prudhoe Bay Crude Oil.

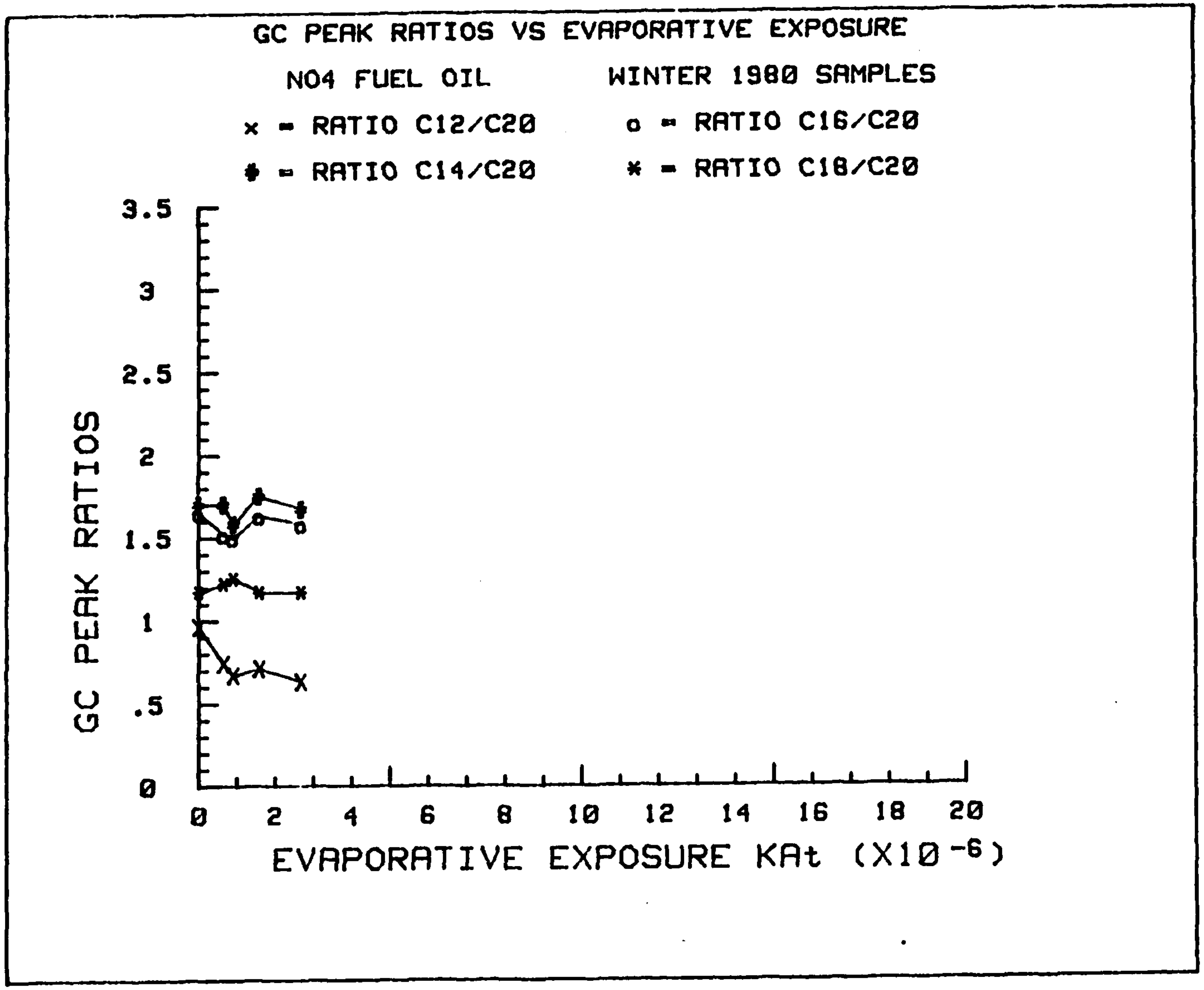

Figure 17a GC Peak Ratios vs. Evaporative Exposure for Winter 1980 Group, No. 4 Fuel Oil.

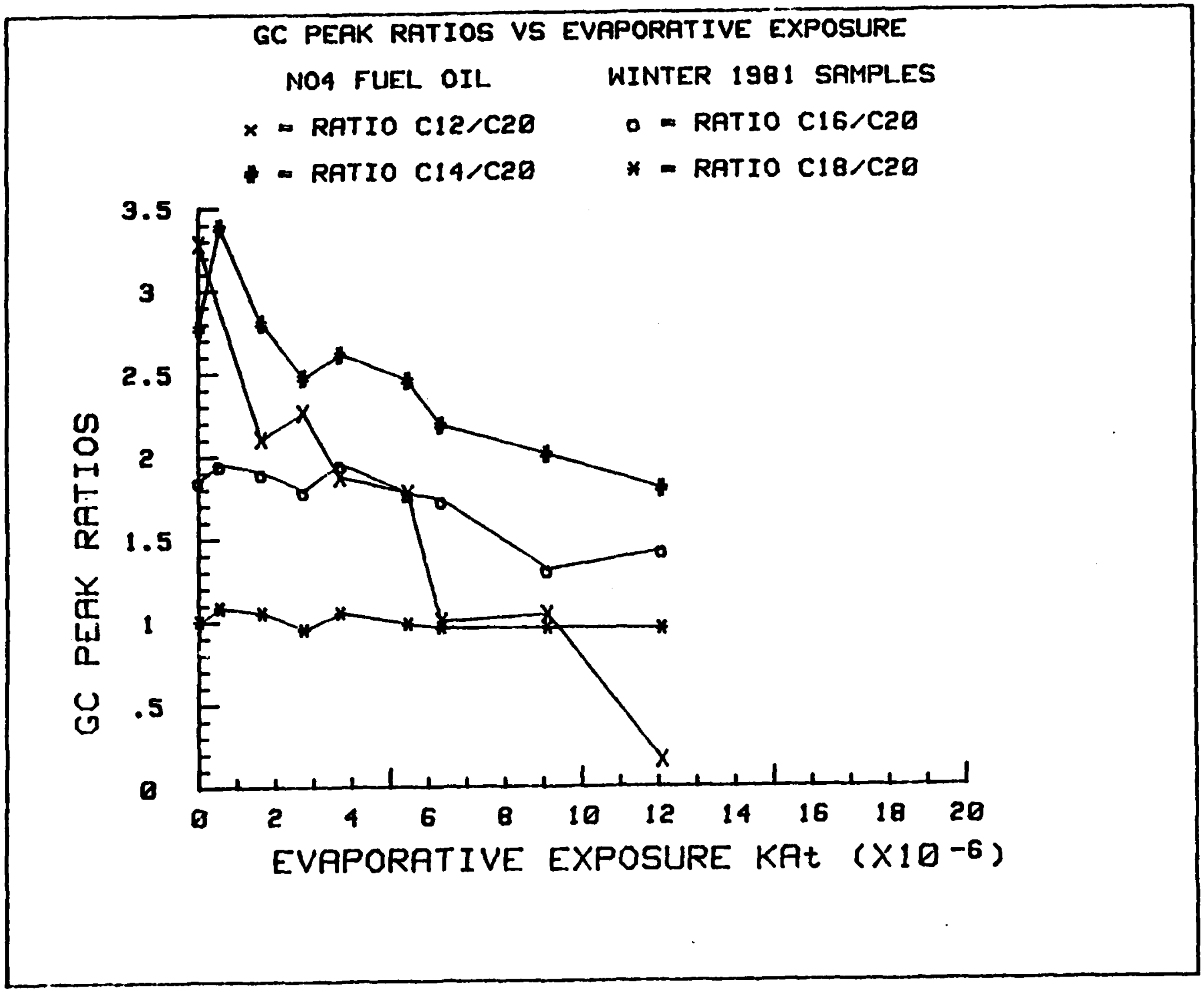

Figure 17b GC Peak Ratios vs. Evaporative Exposure for Winter 1981 Group, No. 4 Fuel Oil.

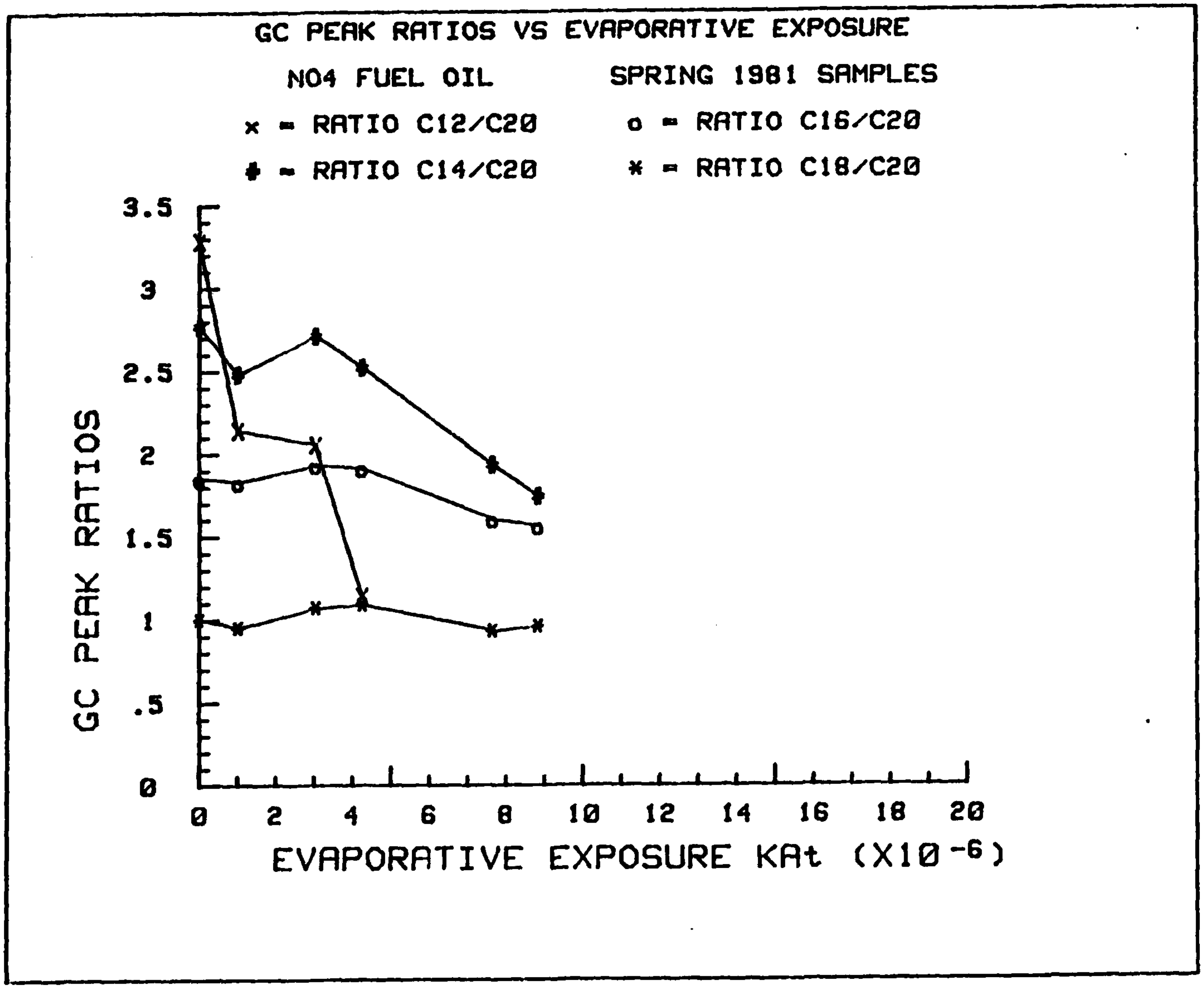

Figure 17c GC Peak Ratios vs. Evaporative Exposure for Spring 1981 Group, No. 4 Fuel Oil.

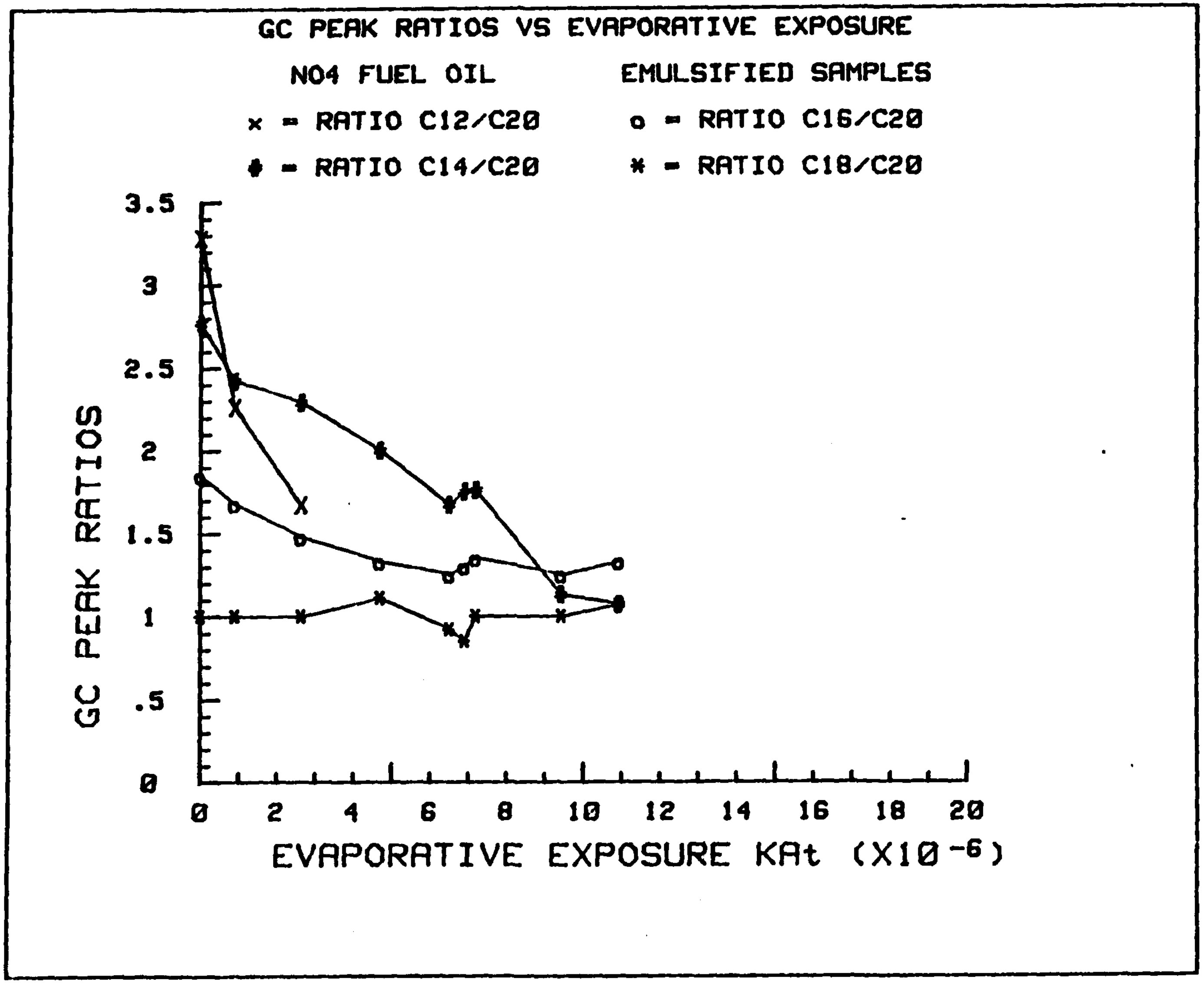

Figure 17d GC Peak Ratios vs. Evaporative Exposure for Emulsified Group, No. 4 Fuel Oil.

no change with evaporative exposure. The pattern is much the same for the Prudhoe Bay crude groups (Figures 16a through 16d) and the No. 4 fuel oil groups (Figures 17a through 17d). The GC scans show a well-defined decrease in the C_{12}/C_{20} ratios for all four groups (Winter 1980, Winter 1981, Spring 1981, and Emulsified), and also a discernible decrease in the C_{14}/C_{20} ratios, particularly for the Spring 1981 and Emulsified groups. The results thus support the concept of using the C_{12}/C_{20} and C_{14}/C_{20} ratios as a weathering index as suggested by Flanigan and Bentz, 1977.

With regard to using these ratios as a quantitative index of evaporative exposure, comparisons of the C_{12}/C_{20} and C_{14}/C_{20} ratio plots for the various sample groups indicate a certain variability in the plots depending on the general weathering conditions. For instance, Figure 18a which shows C_{12}/C_{20} vs. evaporative exposure for all three No. 2 heating oil sample groups, indicates a more rapid decrease in the C_{12}/C_{20} ratios for the Spring 1981 group. Figure 18b, the C_{14}/C_{20} vs. evaporative exposure plots for the No. 2 sample groups, shows far less variability. Figures 19a and 19b show the C_{12}/C_{20} and $C_{14}C_{20}$ plots for the four Prudhoe Bay crude groups. Here there is clearly a significant variability in the decrease rate of the C_{12}/C_{20} and C_{14}/C_{20} ratios within the various groups. The plots for the Winter 1980 and Winter 1981 samples are quite similar. However, the plots for the Spring 1981 groups in both Figures 19a (C_{12}/C_{20}) and 19b (C_{14}/C_{20}) show a sharper rate of decrease than the winter groups. This seems reasonable as the evaporation rate of the oil is dependent on its vapor pressure, which in turn increases with higher spring temperatures. This temperature dependence is not included in the evaporative exposure formulation. More surprising is that the steepest rate of decrease for the Prudhoe Bay crude is in the emulsified groups, which indicates that the emulsification significantly affects the chemical composition as well as the physical properties of the oil. Figures 20a and 20b, the C_{12}/C_{20} and C_{14}/C_{20} plots for No. 4 fuel oil, show somewhat the same trend as with Prudhoe Bay crude except much less pronounced. Of particular interest with the No. 4 fuel oil are the anamolous plots for the Winter 1980 group, which indicate that the results for this group may not be representative of No. 4 fuel oil, and should be regarded as questionable.

In summary, it appears that GC data on the C_{12} and C_{14} peaks do provide an index of the degree of weathering of a particular oil sample. The C_{12}/C_{20} and C_{14}/C_{20} ratios show a well-defined dependence on evaporative exposure, but also reflect changes in the chemical composition of the oil due to the specific environmental conditions under which the weathering occurred. Accordingly, there may be some difficulty in directly referencing C_{12}/C_{20} and C_{14}/C_{20} values to evaporative exposure levels. It may prove more useful to reference physical properties data and combustibility data directly to the C_{12}/C_{20} and C_{14}/C_{20} values, as these values may give a more complete picture of the degree of weathering than evaporative exposure alone. Such cross-referencing would be particularly useful in actual spills where the initial time of the spill (and therefore evaporative exposure levels) is unknown.

6.4 Combustibility Analysis

An important aspect of the sample analysis is the combustibility analysis which focuses on the change in the burnability of the oil with

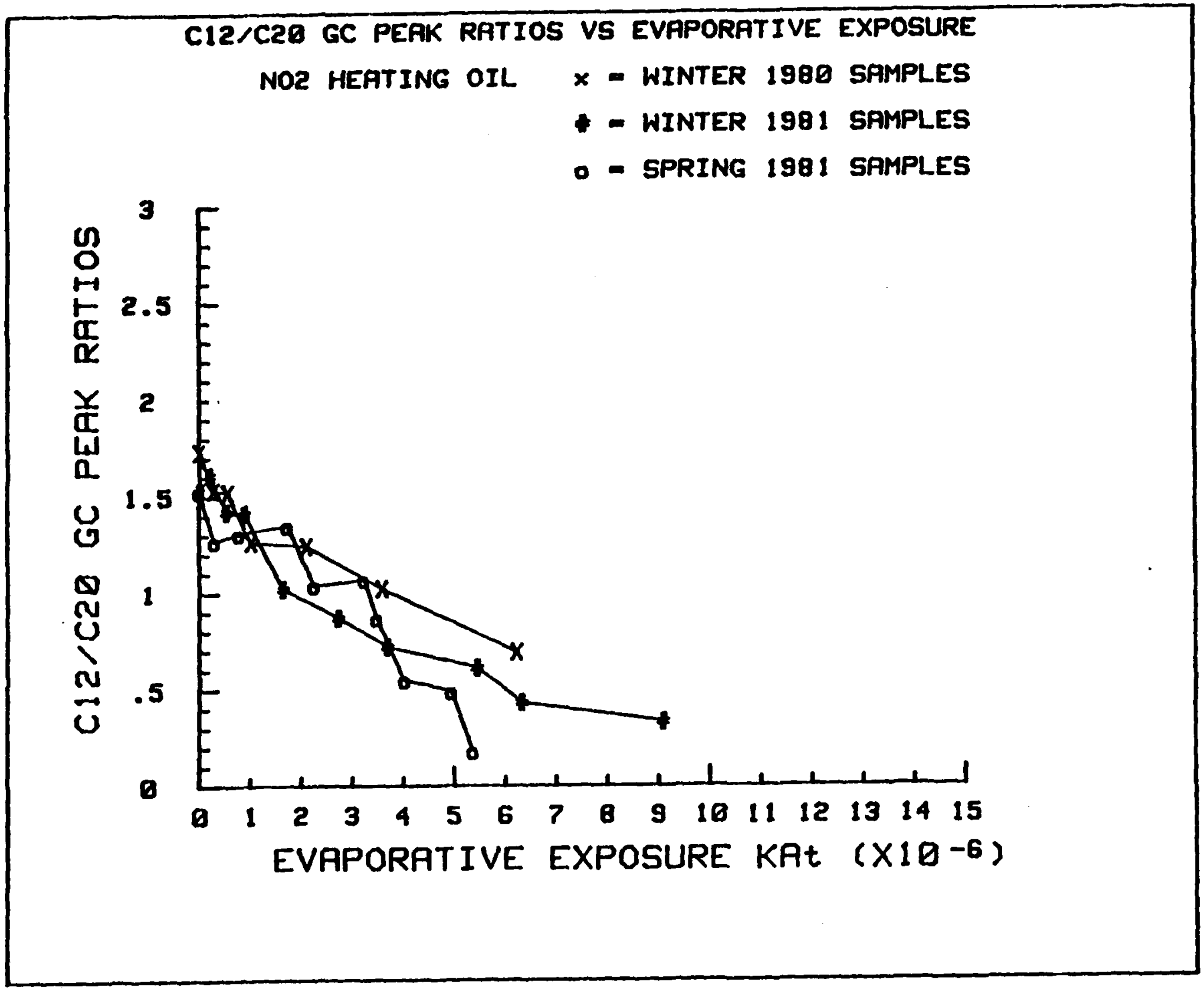

Figure 18a C12/C20 GC Peak Ratios vs. Evaporative Exposure for No. 2 Heating Oil Sample Groups.

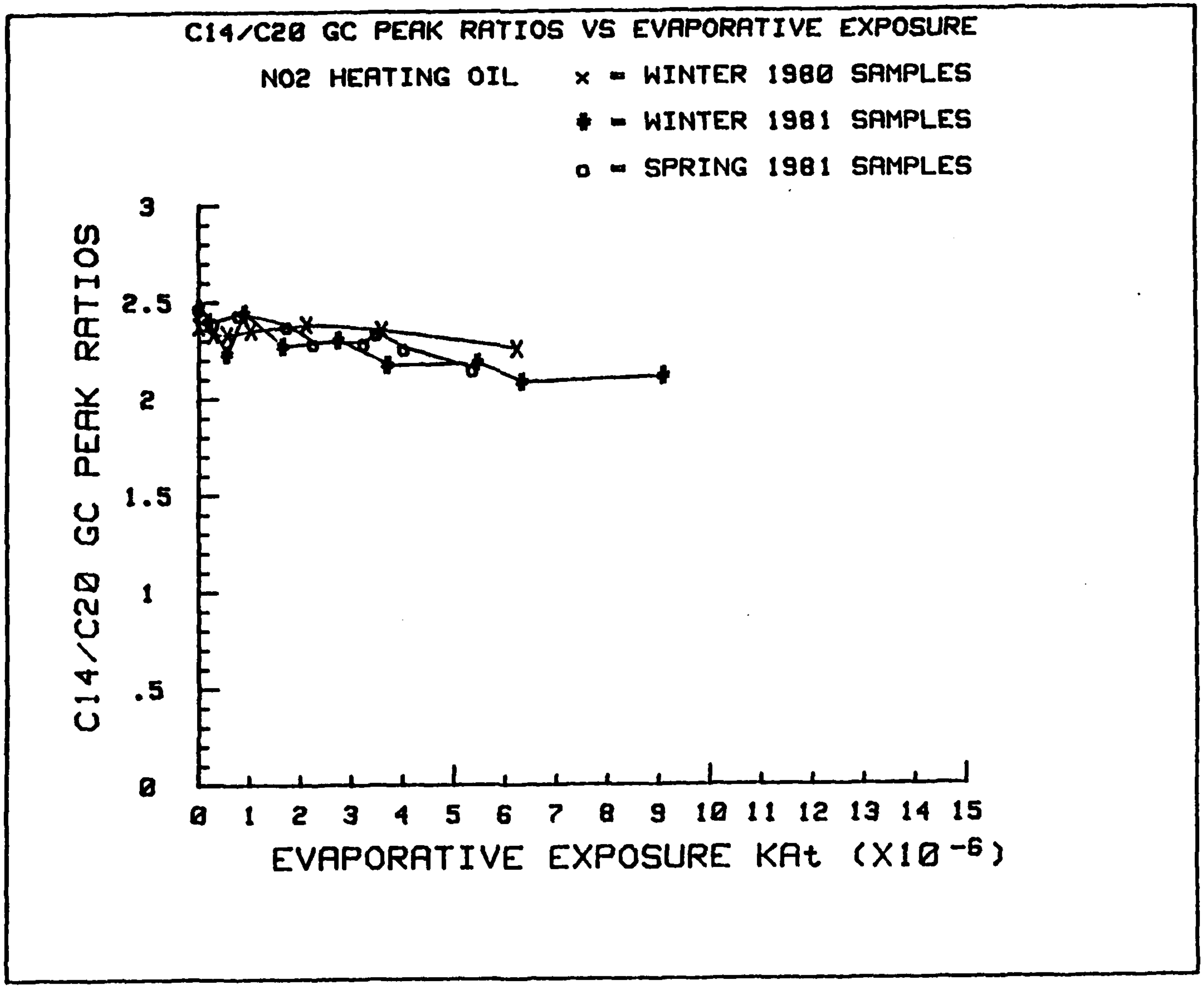

Figure 18b C14/C20 GC Peak Ratios vs. Evaporative Exposure for No. 2 Heating Oil Sample Groups.

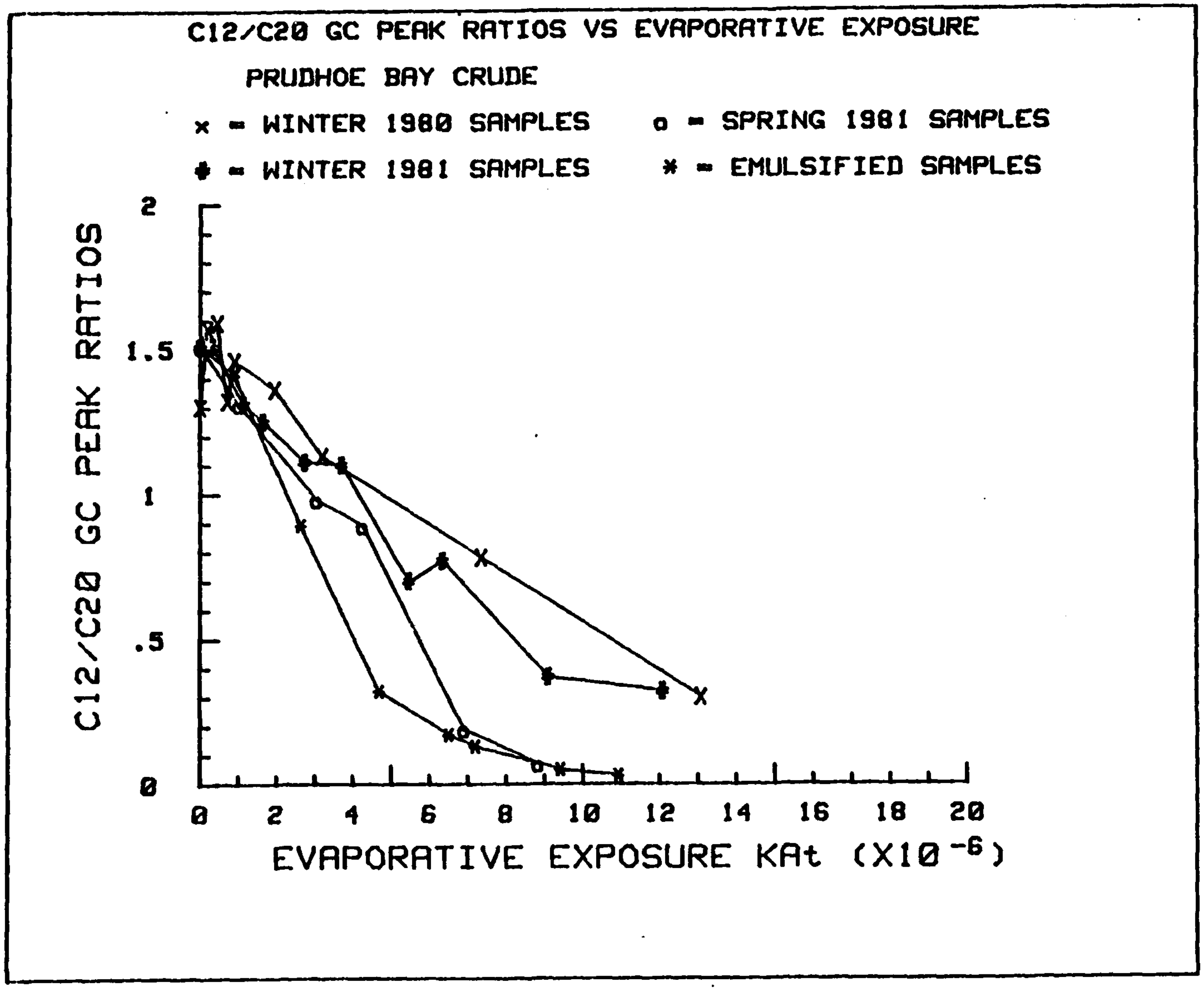

Figure 19a C12/C20 GC Peak Ratios vs. Evaporative Exposure for Prudhoe Bay Crude Oil Sample Groups.

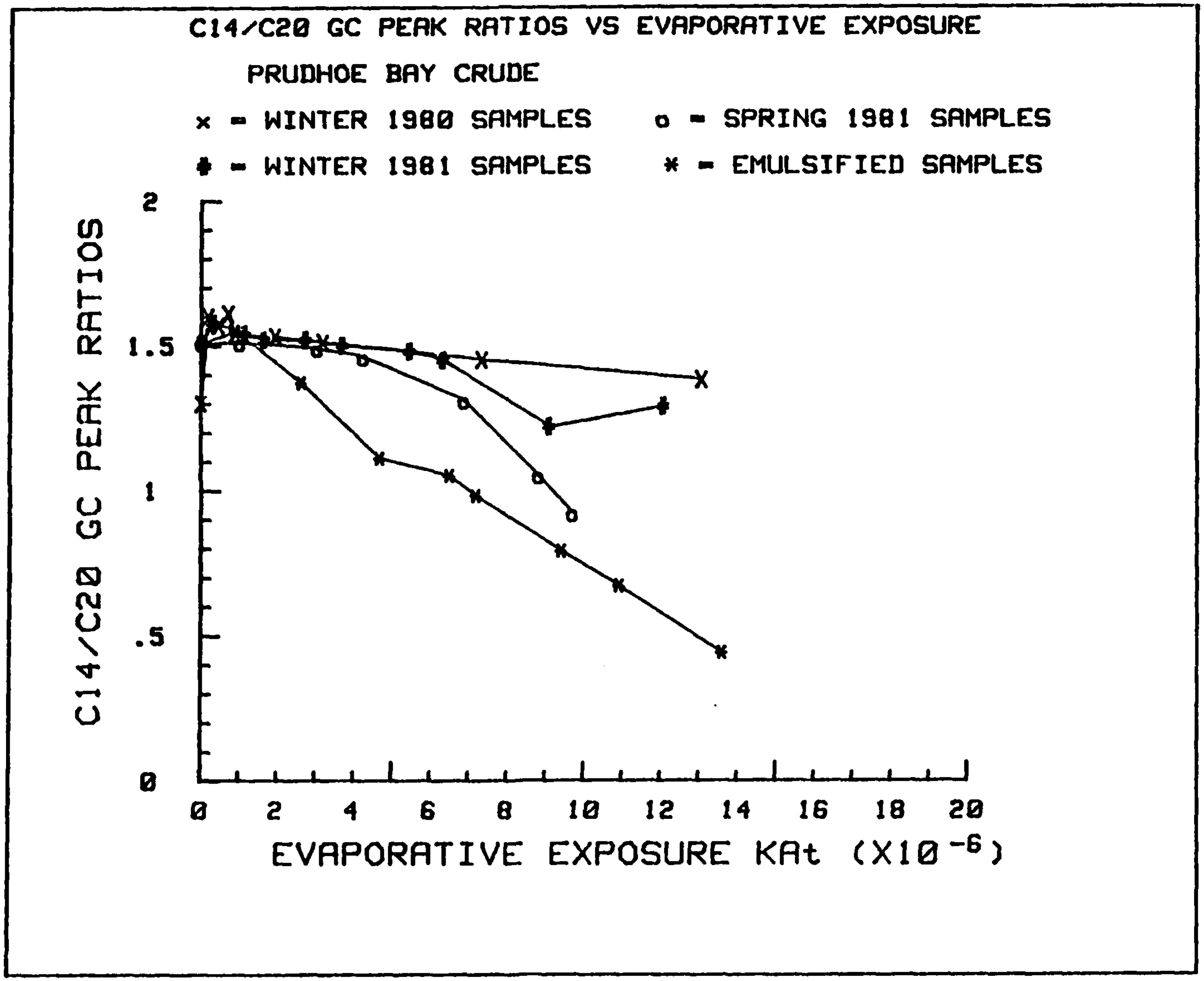

Figure 19b C14/C20 GC Peak Ratios vs. Evaporative Exposure for Prudhoe Bay Crude Oil Sample Groups.

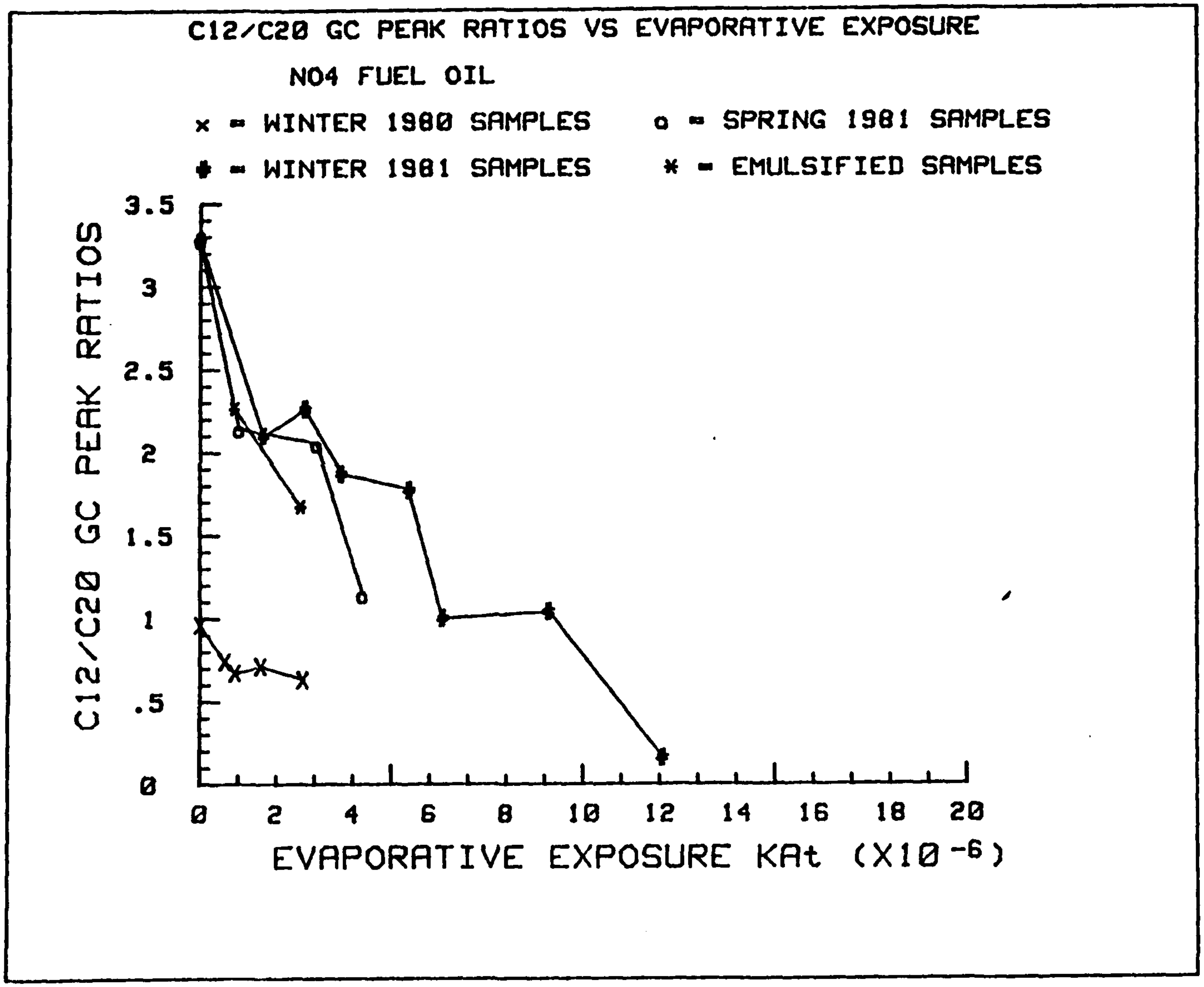

Figure 20a C12/C20 GC Peak Ratios vs. Evaporative Exposure for No. 4 Fuel Oil Sample Groups.

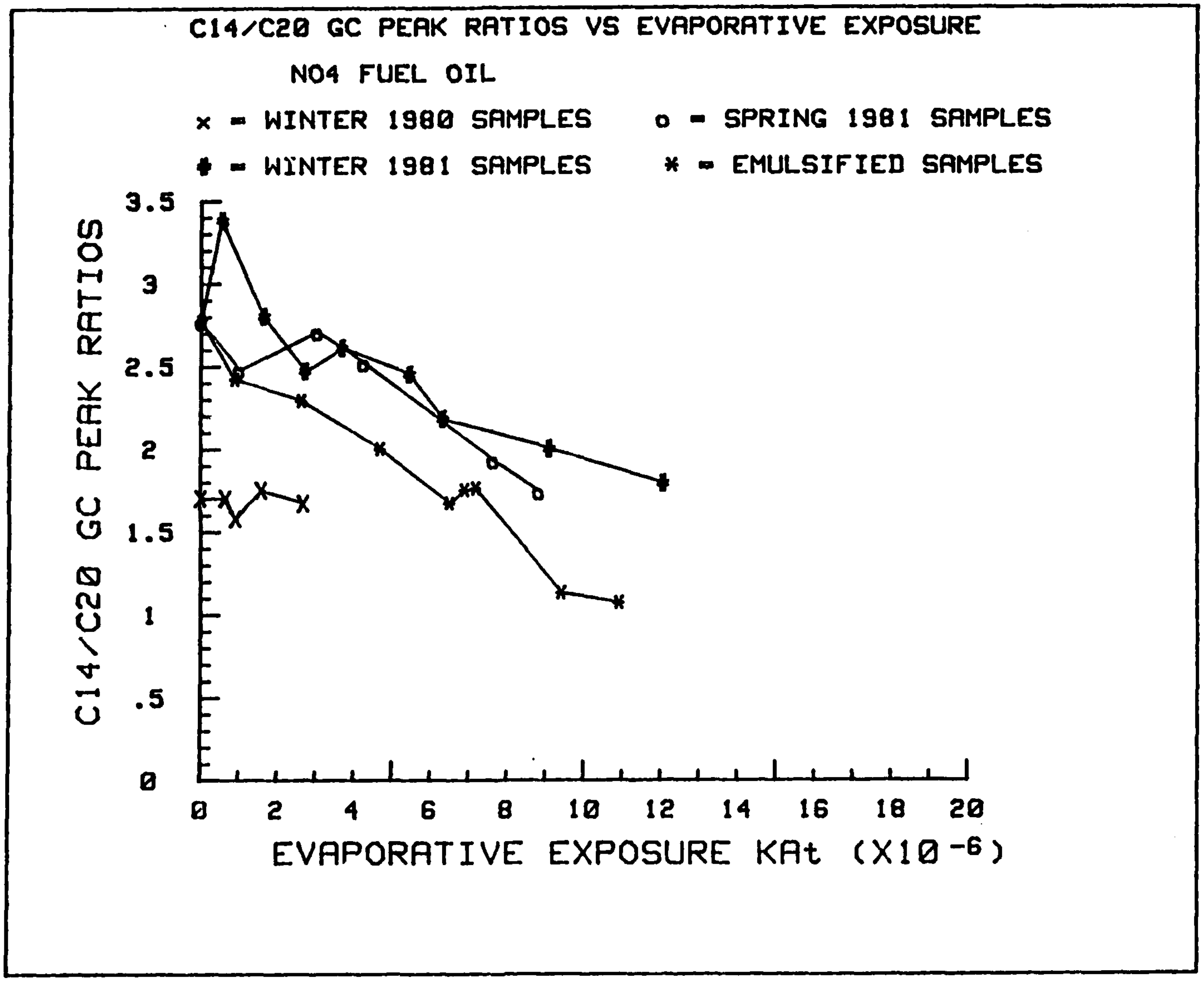

Figure 20b C14/C20 GC Peak Ratios vs. Evaporative Exposure for No. 4 Fuel Oil Sample Groups.

weathering. While containment and recovery of spilled oil is possible under certain ideal conditions, to date there is no consistently effective technique for the cleanup of a large-scale spill in the open ocean. This is particularly true in the Artic where the remoteness and hazardous ice conditions will further hamper any major cleanup effort. Accordingly, current contingency plans for a major spill in the Arctic focus on in-situ combustion as the primary countermeasure.

The combustion of oil spills has been fairly well investigated both theoretically and experimentally. All crude oils and many distillates contain volatile hydrocarbons which burn vigorously when ignited, that is, when the oil is heated to its fire point. The problem with igniting oil on water is that the slick thins out to a point where the heat energy input to initiate combustion is lost to the underlying water (which serves as an infinite heat sink) rather than being conserved within the slick to raise its local temperature to the fire point. The same will be true for an oil spill on ice except that the ice roughness may restrict the spread of the oil, and increase the equilibrium thickness. Ignitability of the spill will also depend on the loss of the volatile components through evaporation, and the presence of water in the oil due to emulsification. Finally, the ignitability of the oil will be affected by local environmental conditions such as ambient temperatures and wind conditions.

Twardus (1979) investigated the effect of weathering on combustibility during a study in which six crude oils and two fuel oils were weathered under winter conditions in Ontario for periods of up to a month. Subsequent sample analysis included flash and fire point determinations, and in-situ combustion tests on open water during which preheating time, ignition time, combustion time, and burning efficiency were measured. The effect of emulsification on combustibility was also investigated by preparing emulsions of the same oils (20% to 70% water content), and conducting the same combustibility determinations. In a companion study, Hossain and Mackay (1979) simulated oil spill combustion with a laboratory apparatus using oil samples from the Twardus experiment, oil samples weathered in a wind tunnel, and a series of prepared emulsions. The combustibility parameters recorded during the laboratory simulations were the same as those recorded by Twardus (1979). In general, both studies provided a broadly consistent picture of the burning characteristics of weathered oils and emulsions. More weathered oils (greater evaporative exposure) required greater ignition times and energies, produced lower oil and flame temperatures, burned longer, and usually produced higher burning efficiencies (about 8% higher) up to a critical exposure value. The tests on the emulsified oils showed that higher water contents led to more difficult igition, shorter burns, lower burning temperatures, and lower burning efficiencies. A particularly surprising outcome of the tests was the higher burning efficiencies with weathering. This is contrary to the idea that combustibility is primarily dependent on the presence of the more volatile fractions, which are rapidly depleted with evaporative exposure. Hossain and Mackay suggested several possible reasons for this, but were unable to pin-point the dominant mechanism.

The combustibility analysis for the R&D Center weathering study included flash and fire point determinations at the R&D Center as outlined in Appendix B, and flash and fire point determinations for selected samples by the University of Toronto (McCurdy et al., 1981). In addition, a series of simple in-situ combustion tests were attempted at the R&D Center to simulate the burning of oil on ice as described in Appendix B. In brief, the tests involved placing the weathered oil samples in an aluminum pan on a block of ice, and heating the samples to ignition with a propane torch. The combustibility parameters recorded included ignition temperature, burn time, and burn efficiency. Photographs of the testing apparatus and a sample burn in progress are shown in Figure 21. Results of the combustibility tests are given in Tables 5a through 5c.

Plots of flash and fire points vs. evaporative exposure for data obtained from the R&D Center analysis for the No. 2 heating oil, Prudhoe Bay crude, and No. 4 fuel oil are shown in Figures 22a and b, 23a and b, and 24a and b respectively. Figures 21a and b indicate that the flash and fire points for the No. 2 heating oil show a small increase with evaporative exposure with values increasing by only 20-30°C over periods of up to 2 weeks. Also note that there is some scatter in the data possibly due to water in the samples or chemical changes not accounted for by the evaporative exposure formulation, but more likely due to errors in the flash and fire point determinations. Figures 22a and b show the flash and fire point plots for Prudhoe Bay crude. These figures show that the Prudhoe Bay crude oil flash and fire points are more sensitive to evaporative exposure with values increasing by 60-70°C over exposure periods of up to a month. This is due to the greater fraction of volatiles present in the crude oil. Again considerable data point scatter is evident in the plots. Flash and fire point plots for the No. 4 fuel oil show trends similar to the No. 2 heating oil with only a moderate increase (20°-40°C) in flash and fire points for exposure periods of up to three weeks. As with the No. 2 oil, this is due to the removal of volatiles from the crude oil during the refining process. Considerable data scatter was again noted.

Figures 25, 26, and 27 show plots of flash and fire points vs. evaporative exposure as determined by the University of Toronto sample analysis for the three oils. Lines have been drawn connecting selected data points to indicate the more or less linear nature of the flash and fire point increase with evaporative exposure. The plots for the No. 2 home heating oil and Prudhoe Bay crude are in agreement with the plots of the R&D Center values showing only a slight flash and fire point dependence on evaporative exposure for the No. 2 heating oil (20°C increase in 10 days), and a sharp increase in flash and fire point with exposure for the Prudhoe Bay crude (40-50°C increase in 20 days). Figure 27 shows that the University of Toronto results for No. 4 fuel oil differ substantially from the R&D Center values showing a 60°C increase in the flash and fire point values with evaporative exposure for exposure periods of up to a month. The reason for this substantial difference in the two sets of values is not immediately clear. Although more data scatter was expected in the R&D Center results, the general trends were expected to be the same.

The results of the in-situ burning tests for the No. 2 home heating oil are given in Table 5a. Plots were not made for No. 2 heating oil as only four data point were obtained as listed in Table 5a, with no clear dependence on the evaporative exposure levels. In fact, of the 14 samples tested, only 4 were successfully ignited. This may be due to the thickness of the oil (only 0.16cm as opposed to 0.32cm for the No. 4 and Prudhoe Bay crude); however, Hossain and Mackay also found this oil difficult to ignite in their laboratory

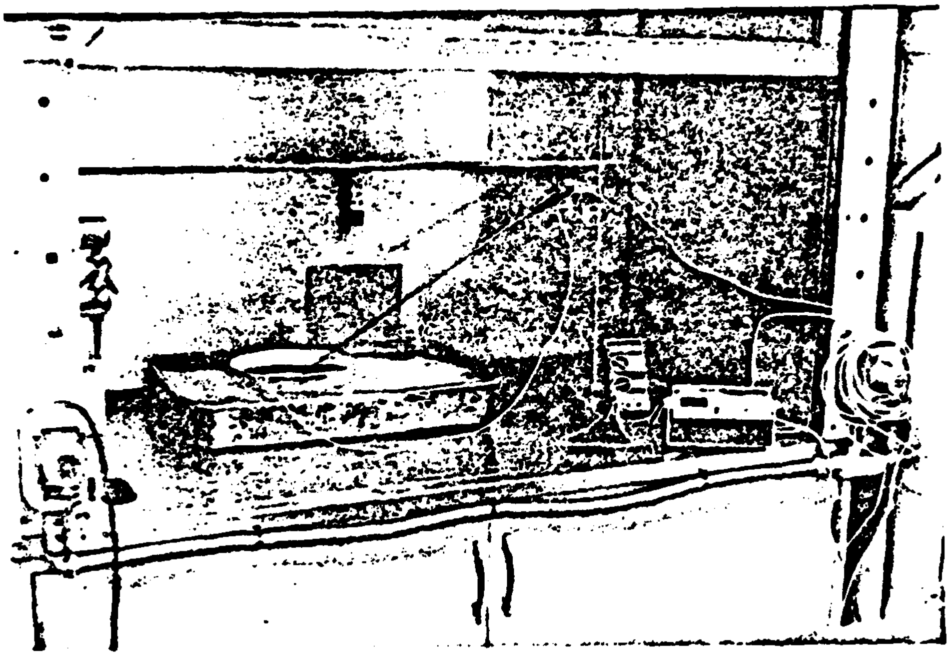

Figure 21a. Photograph showing apparatus for oil/ice combustion tests.

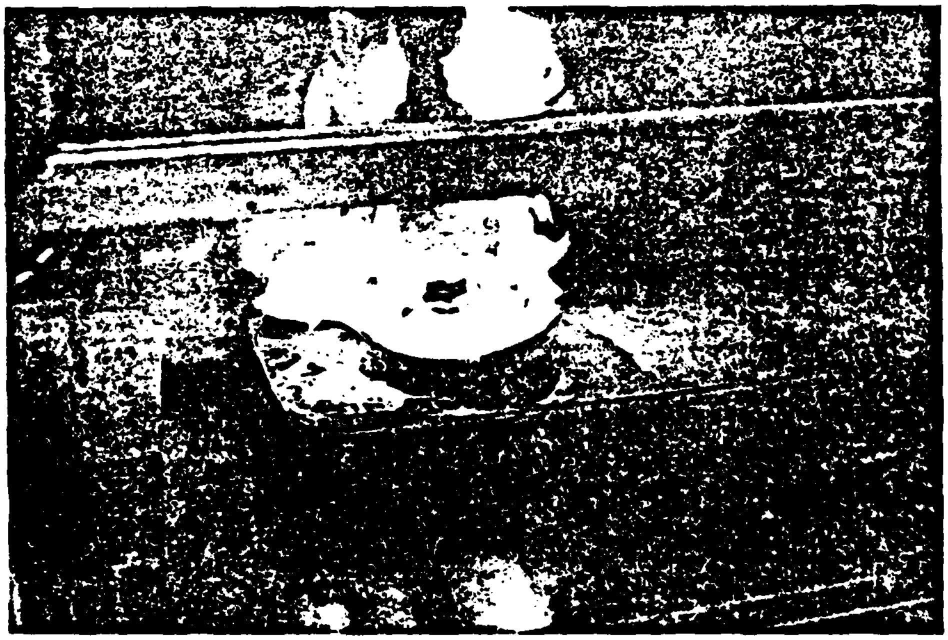

Figure 21b. Photograph showing oil/ice combustion test in progress.

Table 5a Combustibility Data for No.2 Heating Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	FLASH POINT R&DC	FLASH POINT U OF T	FIRE POINT R&DC	FIRE POINT U OF T	IGNITION TEMP DEG C	BURN TIME SECS	BURN EFFICIENCY PERCENT
01	NO2 #01	0.559	112.	——	117.	——	——	——	——
02	NO2 #02	1.021	111.	——	117.	——	——	——	——
03	NO2 #03	2.105	117.	——	126.	——	158.	147.	32.7
04	NO2 #04	3.582	106.	——	110.	——	156.	32.	6.5
05	NO2 #05	6.219	121.	——	129.	——	——	——	0.0 *
06	NO2 #06	0.000	——	——	——	——	——	——	——
07	NO2 #07	0.278	122.	——	127.	——	——	——	——
08	NO2 #08	0.547	——	——	——	——	——	——	0.0 *
09	NO2 #09	1.645	——	——	——	——	——	——	0.0 *
10	NO2 #10	2.730	——	108.	——	114.	——	——	0.0 *
11	NO2 #11	3.693	——	——	——	——	——	——	——
12	NO2 #12	5.450	——	——	——	——	——	——	——
13	NO2 #13	6.325	——	——	——	——	——	——	——
14	NO2 #14	9.090	——	110.	——	115.	——	——	——
15	NO2 #15	12.072	——	——	——	——	——	——	——
16	NO2 #16	0.896	130.	128.	132.	131.	——	——	0.0 *
17	NO2 #17	2.631	——	——	——	——	——	——	——
18	NO2 #18	0.200	——	——	——	——	——	——	——
19	NO2 #19	0.305	113.	——	114.	——	142.	16.	6.9
20	NO2 #20	0.787	112.	107.	126.	116.	——	——	0.0 *
21	NO2 #21	2.250	118.	107.	136.	113.	——	——	0.0 *
22	NO2 #22	3.633	128.	115.	138.	121.	——	——	——
23	NO2 #23	4.951	——	——	——	——	——	——	——
24	NO2 #24	5.366	——	125.	——	132.	——	——	——
25	NO2 #25	6.566	——	——	——	——	——	——	——
26	NO2 #26	13.584	——	——	——	——	——	——	——
27	NO2 #27	1.739	114.	——	120.	——	——	——	0.0 *
28	NO2 #28	3.235	128.	123.	136.	131.	——	——	0.0 *
29	NO2 #29	3.484	126.	——	130.	——	——	——	0.0 *
30	NO2 #30	4.016	132.	——	138.	——	——	——	0.0 *
31	NO2 ST1	0.000	86.	——	102.	——	396.	153.	43.2
32	NO2 ST2	0.000	——	104.	——	109.	——	——	——
33	NO2 ST3	0.000	——	——	——	——	——	——	——

* Indicates Combustion Test With No Ignition

Table 5b Combustibility Data for Prudhoe Bay Crude Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	FLASH POINT R&DC	FLASH POINT U OF T	FIRE POINT R&DC	FIRE POINT U OF T	IGNITION TEMP DEG C	BURN TIME SECS	BURN EFFICIENCY PERCENT
01	PBC #01	0.449	——	——	——	——	——	——	——
02	PBC #02	0.887	——	——	——	——	——	——	——
03	PBC #03	1.947	87.	——	95.	——	120.	216.	29.2
04	PBC #04	3.188	125.	——	154.	——	127.	114.	16.2
05	PBC #05	7.335	134.	——	149.	——	182.	91.	5.6
06	PBC #06	13.071	137.	——	150.	——	——	——	——
07	PBC #07	0.185	96.	——	107.	——	——	——	——
08	PBC #08	0.707	99.	——	117.	——	——	——	——
09	PBC #09	0.320	104.	——	112.	——	——	——	——
10	PBC #10	1.068	——	——	——	——	——	——	——
11	PBC #11	1.134	——	——	——	——	——	——	——
12	PBC #12	1.645	104.	101.	124.	122.	——	——	——
13	PBC #13	2.730	104.	——	134.	——	137.	25.	3.2
14	PBC #14	3.693	108.	112.	138.	130.	——	——	——
15	PBC #15	5.450	108.	——	156.	——	——	——	——
16	PBC #16	6.325	138.	——	146.	——	——	——	——
17	PBC #17	9.090	152.	——	178.	——	——	——	——
18	PBC #18	12.072	——	——	——	——	——	——	0.0 *
19	PBC #19	0.896	——	——	——	——	86.	241.	32.3
20	PBC #20	2.631	——	——	——	——	——	——	——
21	PBC #21	4.685	——	——	——	——	——	——	0.0 *
22	PBC #22	6.494	——	——	——	——	——	——	0.0 *
23	PBC #23	7.189	——	——	——	——	——	——	0.0 *
24	PBC #24	9.418	——	——	——	——	——	——	——
25	PBC #25	10.926	——	——	——	——	——	——	——
26	PBC #26	1.011	124.	110.	136.	128.	——	——	——
27	PBC #27	3.042	——	——	——	——	——	——	——
28	PBC #28	4.250	146.	——	152.	——	——	——	——
29	PBC #29	7.071	——	——	——	——	——	——	——
30	PBC #30	8.829	——	——	——	——	——	——	——
31	PBC #31	6.895	——	——	——	——	——	——	——
32	PBC #32	7.651	182.	——	184.	——	——	——	——
33	PBC #33	9.713	——	150.	——	171.	——	——	——
34	PBC #34	13.605	——	——	——	——	——	——	0.0 *
35	PBC #35	17.443	——	——	——	——	——	——	0.0 *
36	PBC ST1	0.000	104.	——	128.	——	87.	247.	35.3
37	PBC ST2	0.000	84.	——	116.	——	——	——	——
38	PBC ST3	0.000	82.	——	104.	——	——	——	——

* Indicates Combustion Test With No Ignition.

Table 5c Combustibility Data for No.4 Fuel Oil.

#	SAMPLE	EVAP EXPOSURE X 10^{-6}	FLASH POINT R&DC	FLASH POINT U OF T	FIRE POINT R&DC	FIRE POINT U OF T	IGNITION TEMP DEG C	BURN TIME SECS	BURN EFFICIENCY PERCENT
01	NO4 #01	0.645	138.	—	152.	—	—	—	—
02	NO4 #02	0.906	—	—	—	—	—	—	0.0 *
03	NO4 #03	1.579	150.	—	168.	—	269.	235.	66.7
04	NO4 #04	2.677	—	—	—	—	270.	262.	58.1
05	NO4 #05	0.784	120.	—	132.	—	—	—	—
06	NO4 #06	1.493	128.	—	138.	—	—	—	—
07	NO4 #07	0.547	—	103.	116.	110.	—	—	—
08	NO4 #08	1.645	109.	—	122.	—	166.	46.	7.0
09	NO4 #09	2.730	—	—	116.	—	85.	342.	36.5
10	NO4 #10	3.693	122.	117.	126.	121.	—	—	—
11	NO4 #11	5.450	128.	—	134.	—	—	—	—
12	NO4 #12	6.325	132.	128.	136.	132.	—	—	—
13	NO4 #13	9.090	124.	—	126.	—	—	—	—
14	NO4 #14	12.072	—	148.	158.	152.	—	—	—
15	NO4 #15	0.896	—	98.	—	102.	85.	285.	44.4
16	NO4 #16	2.631	—	—	—	—	—	—	0.0 *
17	NO4 #17	4.685	—	—	—	—	—	—	0.0 *
18	NO4 #18	6.494	—	—	—	—	—	—	—
19	NO4 #19	7.189	—	—	—	—	—	—	0.0 *
20	NO4 #20	9.418	—	—	—	—	—	—	0.0 *
21	NO4 #21	10.926	—	—	—	—	—	—	0.0 *
22	NO4 #22	1.011	108.	—	117.	—	120.	315.	36.0
23	NO4 #23	3.042	—	—	—	—	109.	220.	37.3
24	NO4 #24	4.250	—	—	—	—	—	—	—
25	NO4 #25	7.071	—	—	—	—	—	—	0.0 *
26	NO4 #26	8.829	—	—	—	—	—	—	—
27	NO4 #27	6.895	—	—	—	—	—	—	—
28	NO4 #28	7.651	—	—	—	—	—	—	—
29	NO4 #29	9.713	—	—	—	—	—	—	0.0 *
30	NO4 #30	13.605	—	—	—	—	—	—	0.0 *
31	NO4 #31	17.443	—	—	—	—	—	—	0.0 *
32	NO4 ST1	0.000	140.	—	142.	—	275.	219.	63.6
33	NO4 ST2	0.000	108.	78.	119.	84.	211.	197.	34.4
34	NO4 ST3	0.000	111.	—	114.	—	—	—	—

* Indicates Combustion Test With No Ignition.

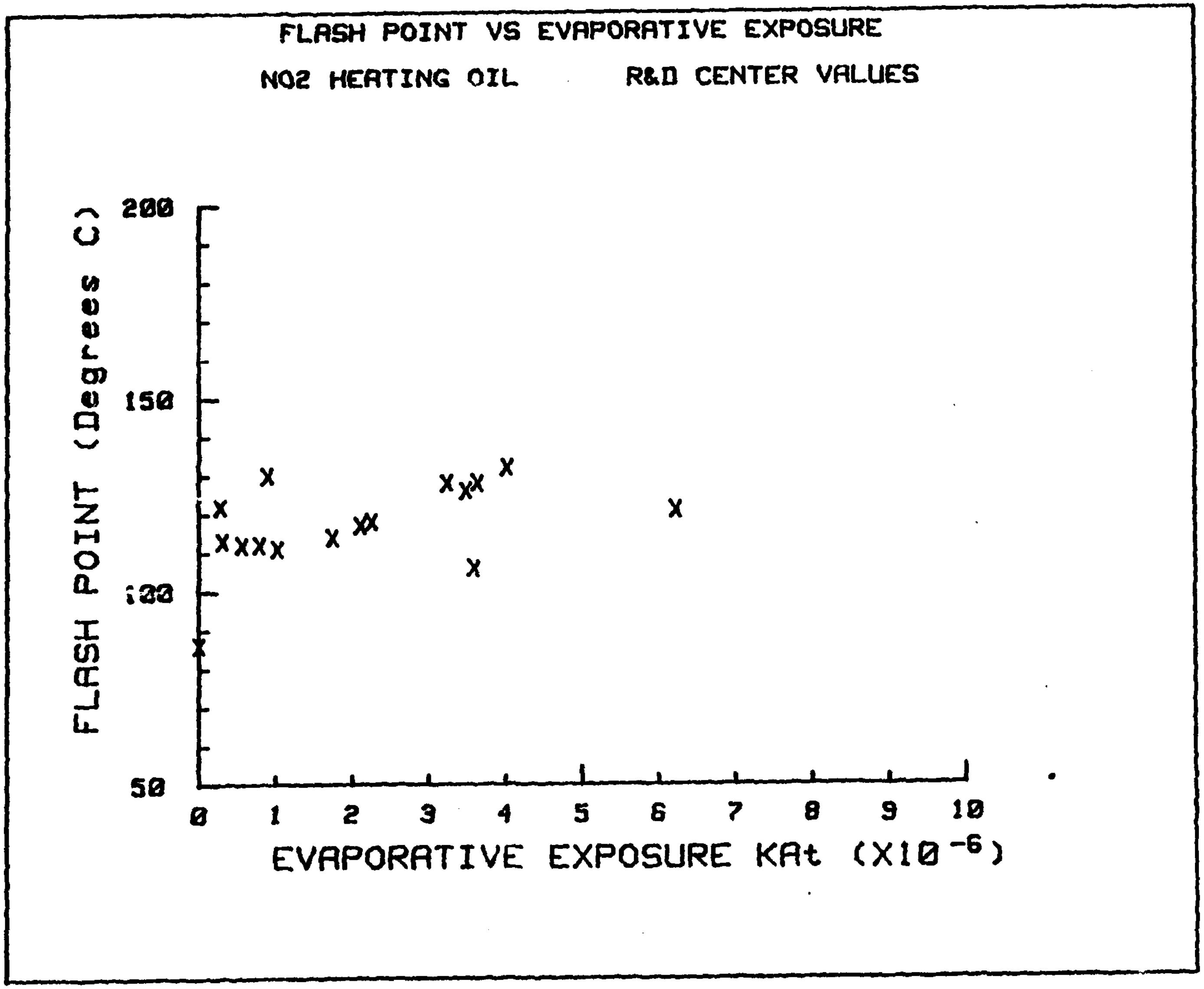

Figure 22a Flash Point vs. Evaporative Exposure for No. 2. Heating Oil (R&D Center Values).

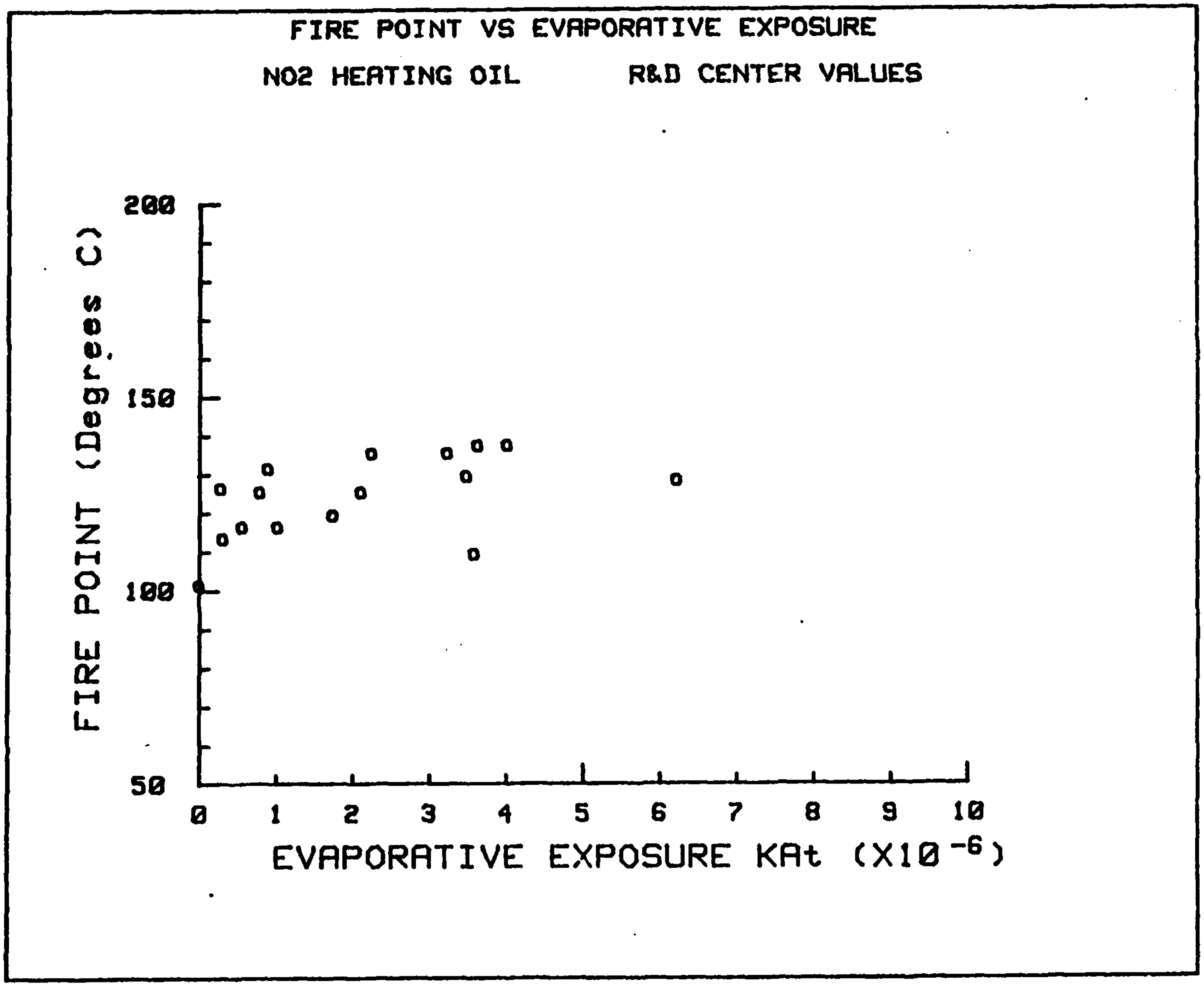

Figure 22b Fire Point vs. Evaporative Exposure for No. 2 Heating Oil (R&D Center Values).

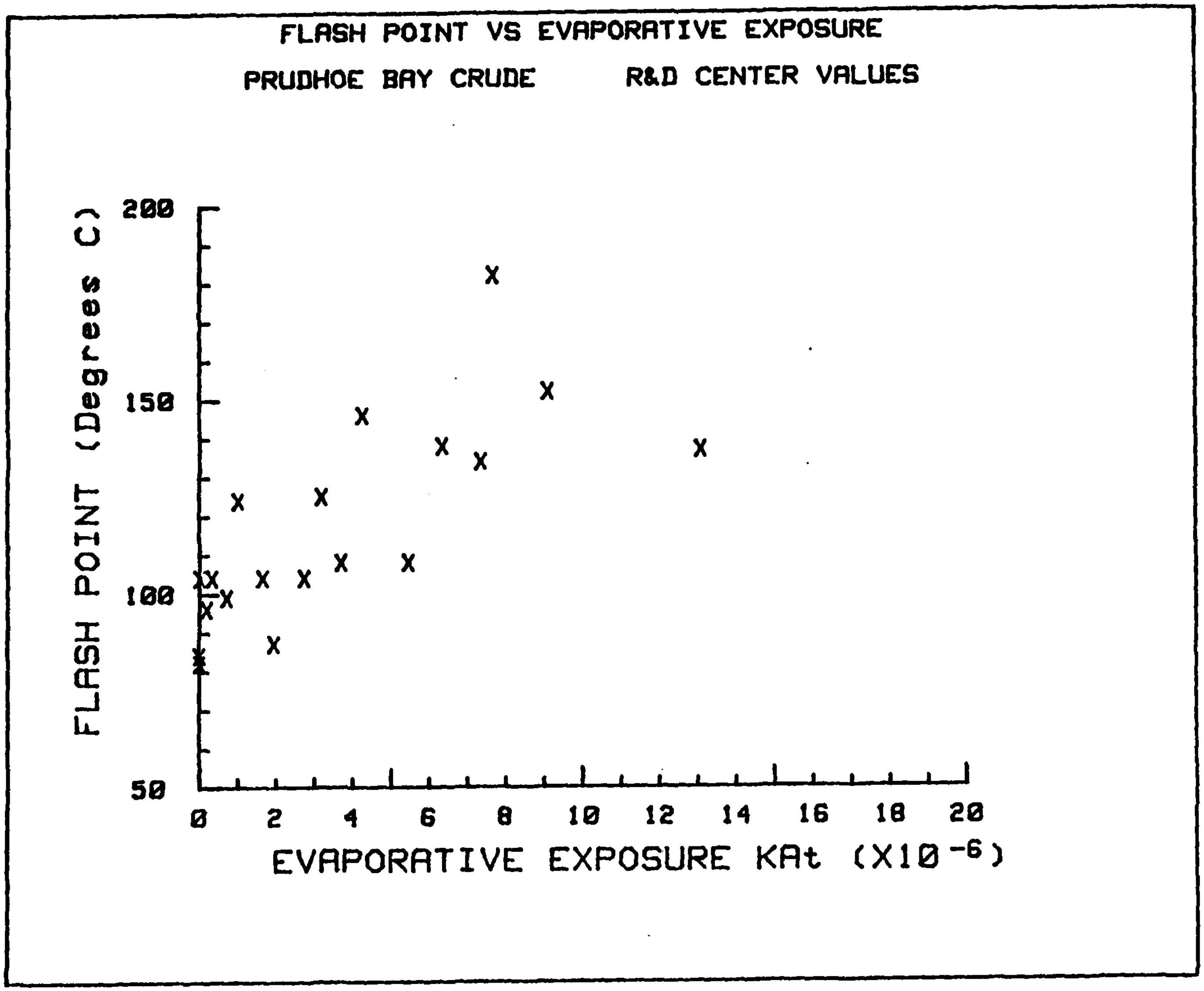

Figure 23a Flash Point vs. Evaporative Exposure for Prudhoe Bay Crude Oil (R&D Center Values).

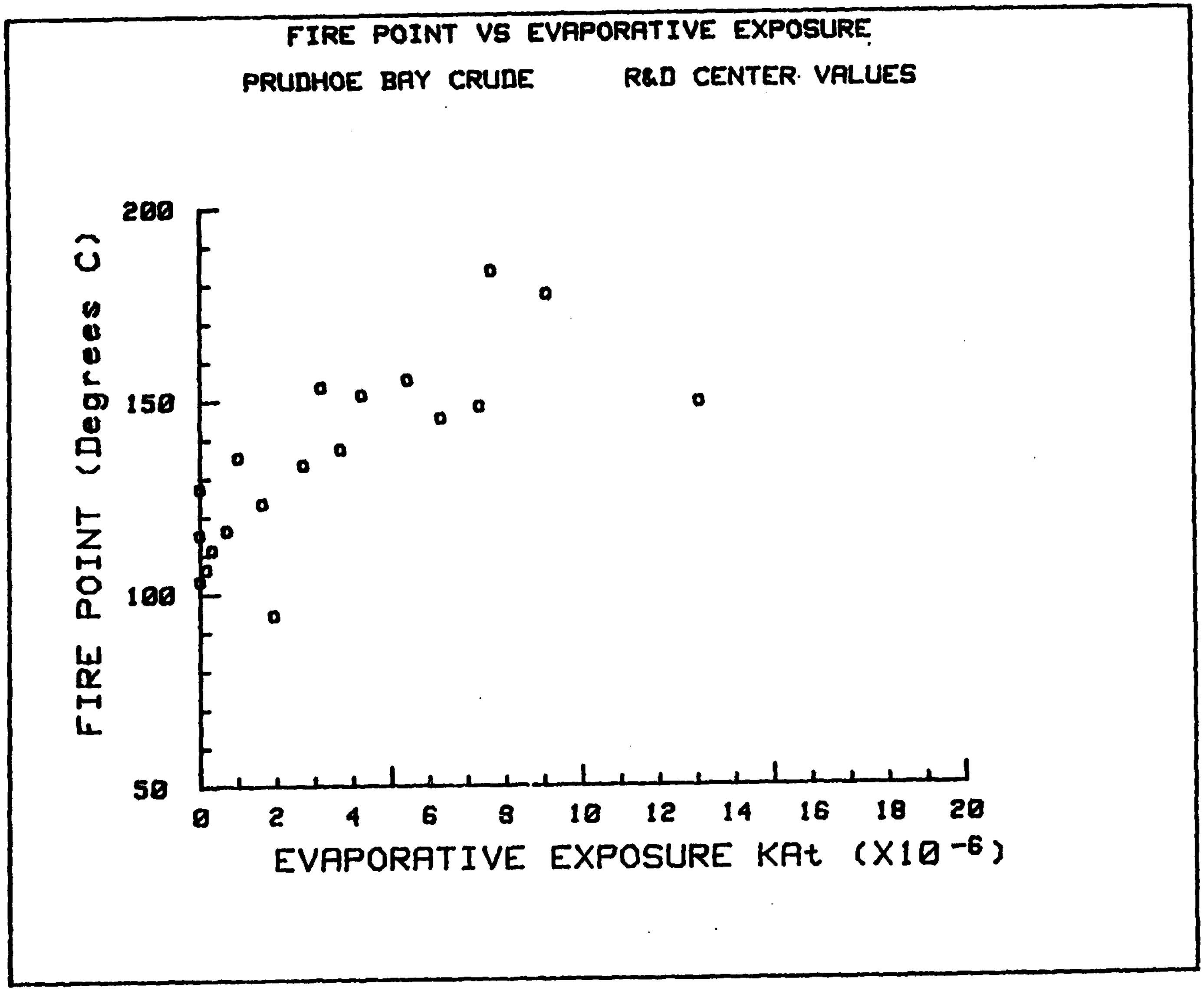

Figure 23b Fire Point vs. Evaporative Exposure for Prudhoe Bay Crude Oil (R&D Center Values).

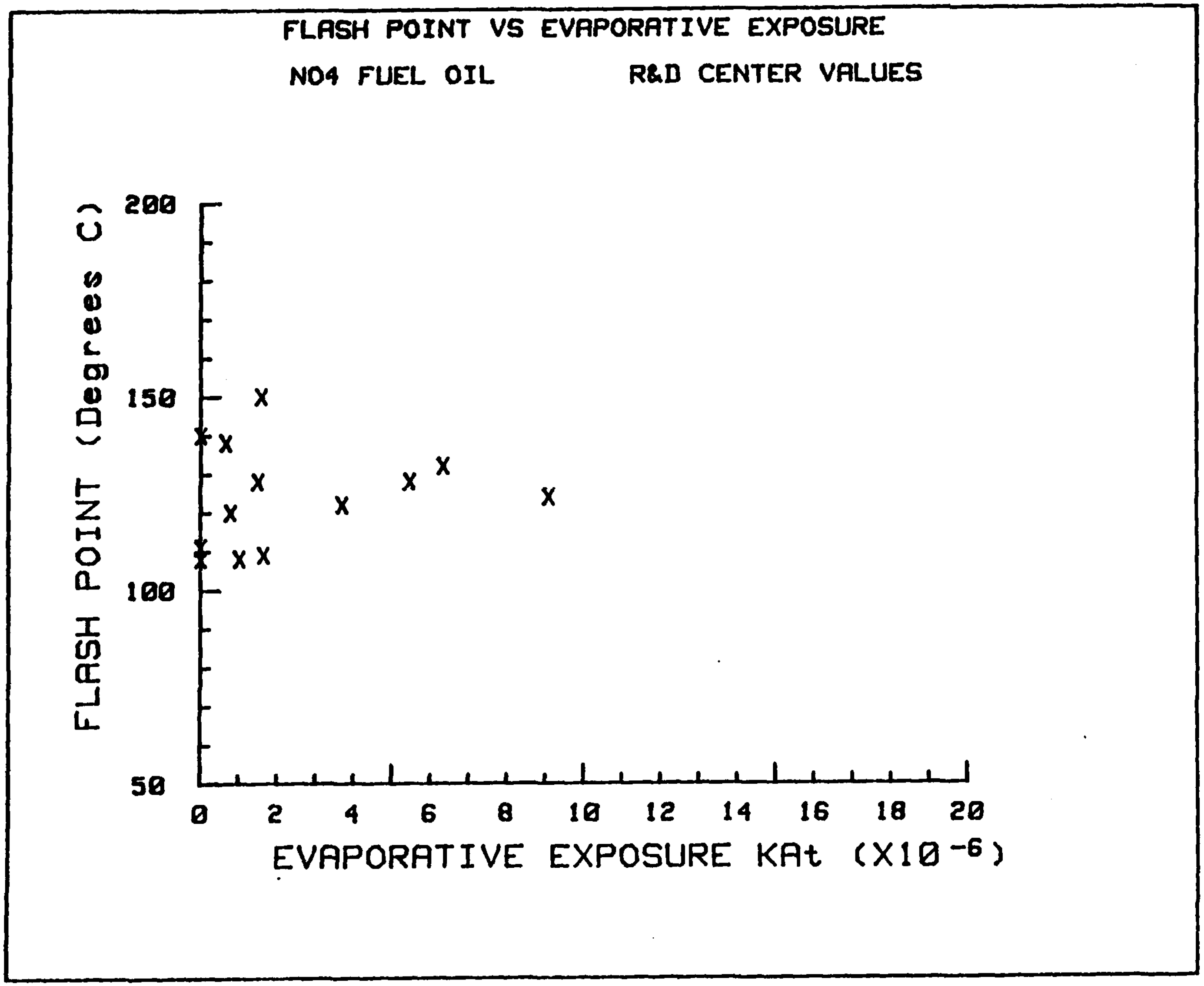

Figure 24a Flash Point vs. Evaporative Exposure for No. 4 Fuel Oil (R&D Center Values).

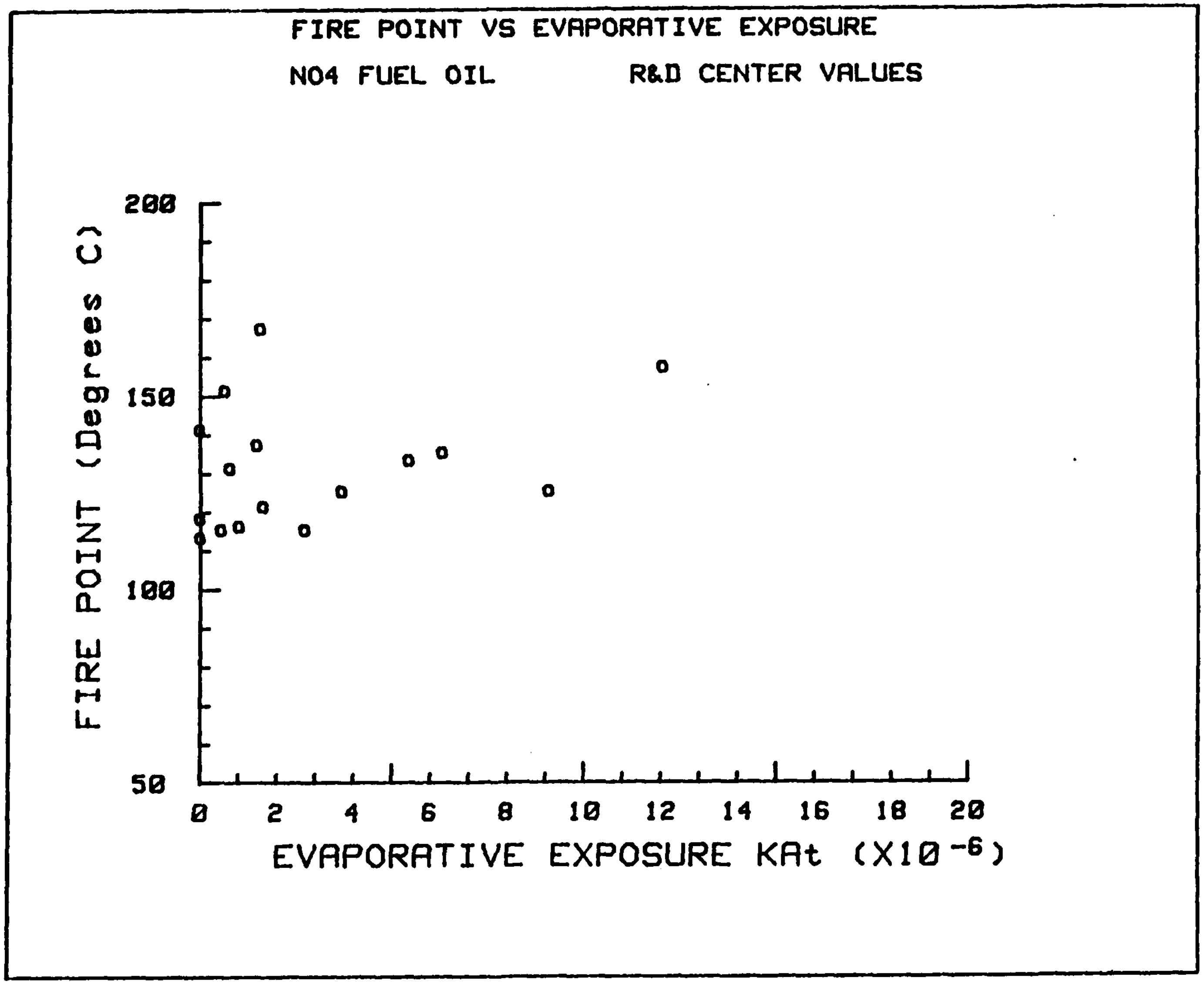

Figure 24b Fire Point vs. Evaporative Exposure for No. 4 Fuel Oil (R&D Center Values).

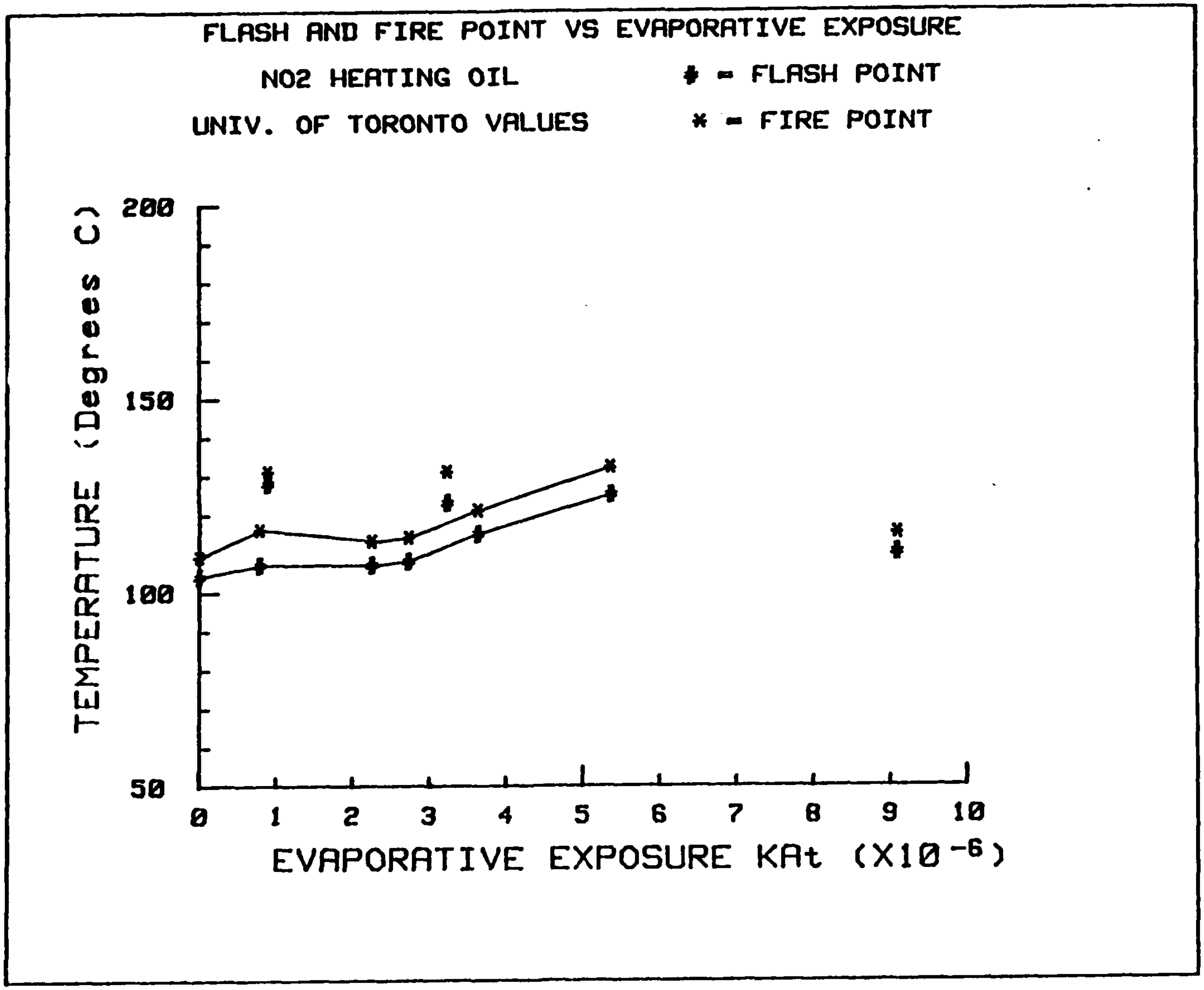

Figure 25 Flash and Fire Point vs. Evaporative Exposure for No. 2 Heating Oil (Univ. of Toronto Values).

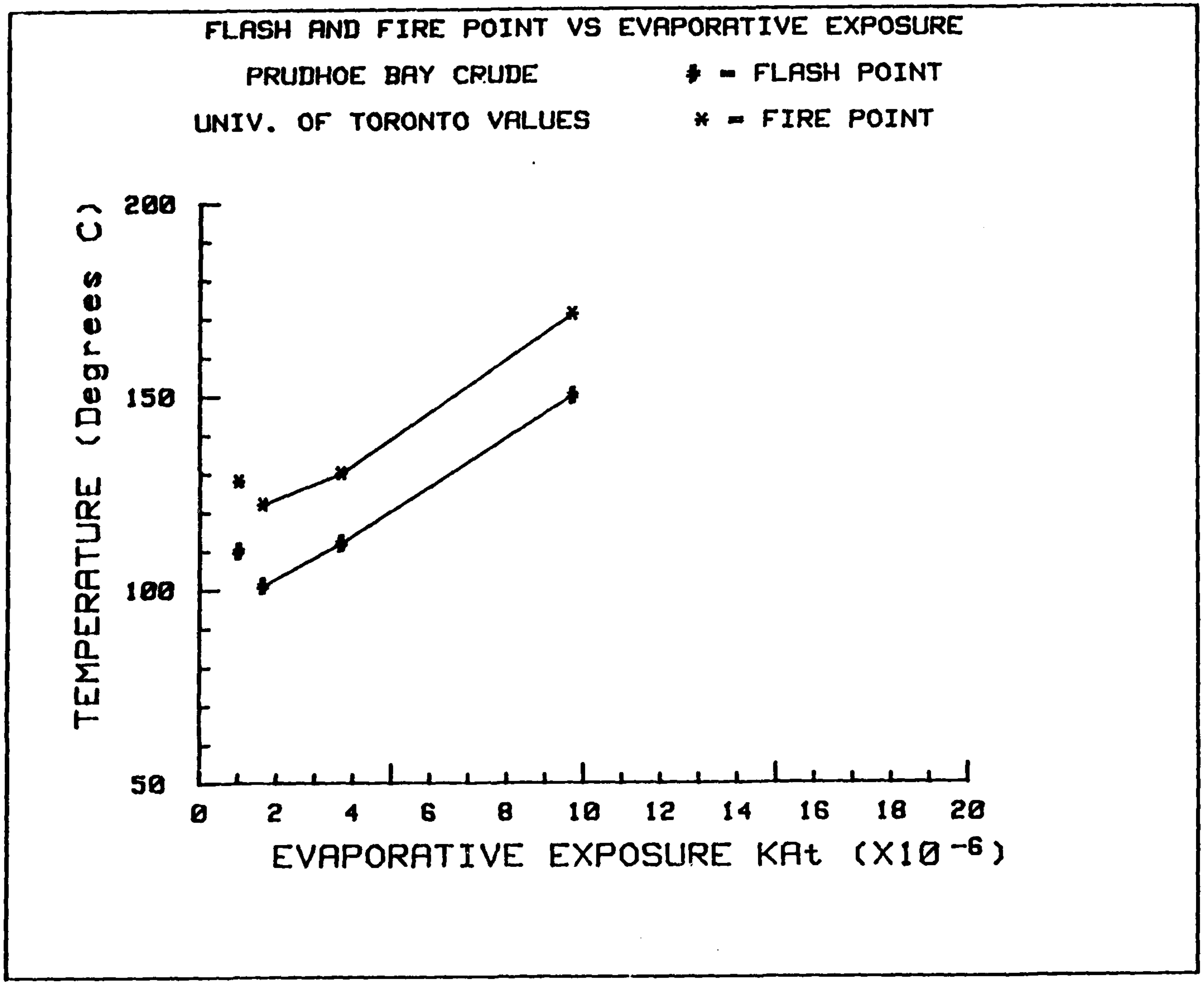

Figure 26 Flash and Fire Point vs. Evaporative Exposure for Prudhoe Bay Crude Oil (Univ. of Toronto Values).

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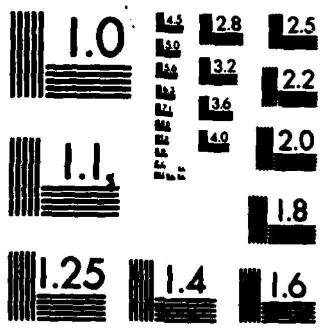

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

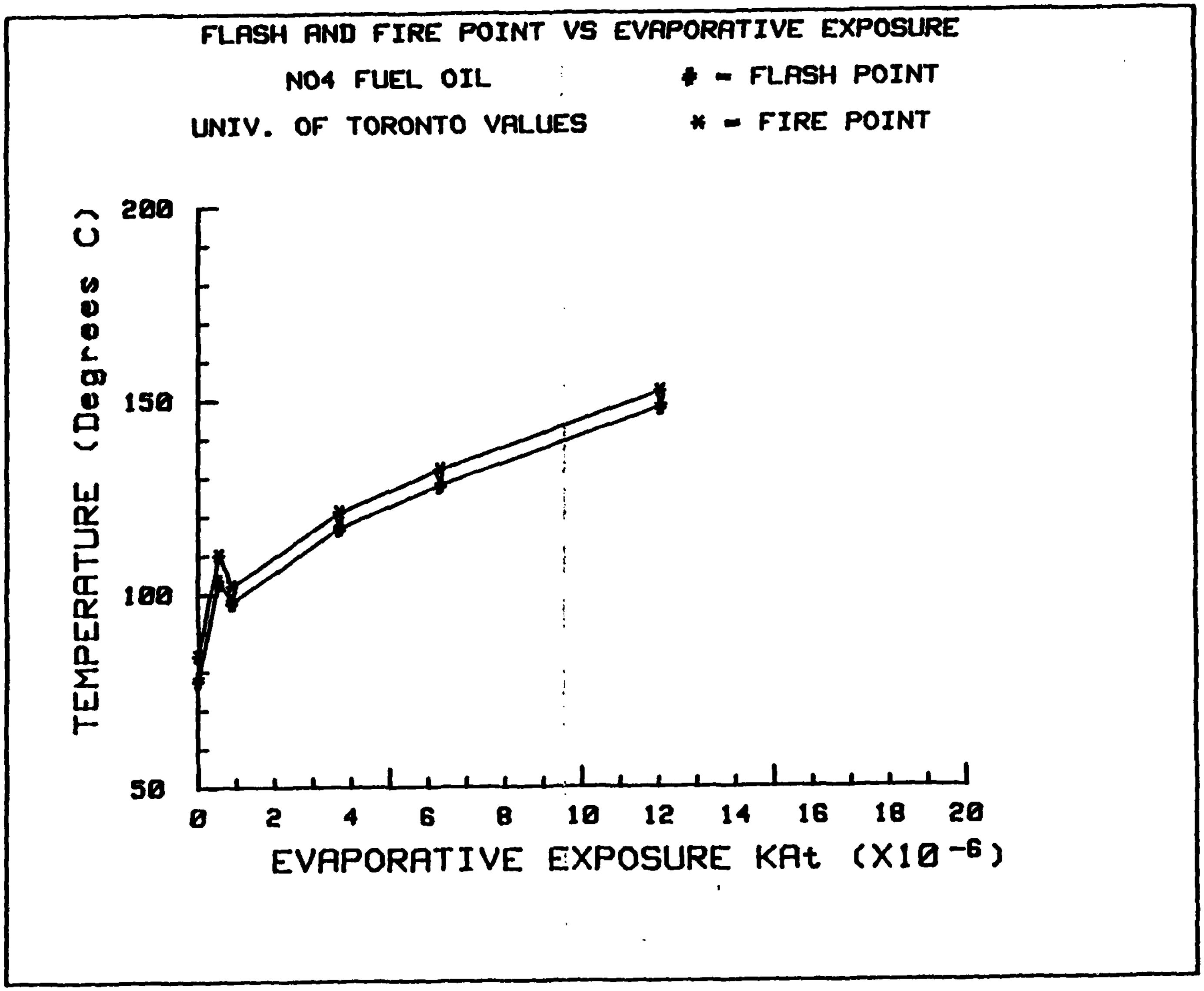

Figure 27 Flash and Fire Point vs. Evaporative Exposure for No. 4 Fuel Oil (Univ. of Toronto Values).

apparatus. Certainly the insensitivity of the combustibility parameters to evaporative exposure is consistent with the flash point results.

Prudhoe Bay crude samples were easier to ignite, with ignition obtained for 6 out of the 11 samples tested. Examination of the corresponding evaporative exposure values indicate that the Prudhoe Bay crude samples were burnable up to evaporative exposure values of about 7×10^6 (two weeks exposure under winter conditions), providing the sample was not emulsified. Figures 28a through c give plots of ignition temperature, burn time, and burn efficiency for the Prudhoe Bay crude samples. Selected data points have been joined with lines to indicate general trends. Although the data is quite limited, the results seem to indicate an increase in ignition temperature, decrease in burn time, and decrease in burning efficiency with evaporative exposure. These decrease in burn time and burning efficiency is opposite to the trend identified by Hossain and Mackay.

Combustibility test results for the No. 4 fuel oil are given in Table 5c. For this oil, 8 samples were ignited out of the 18 tested with the limiting evaporative exposure value again somewhere around 7×10^6 (i.e. two weeks exposure) for unemulsified samples. Figures 29a through c give plots of ignition time, burn times, and burning efficiency vs. evaporative exposure for the No. 4. In contrast to the Prudhoe Bay crude, the No. 4 fuel oil combustibility parameter plots show no well-defined trend in relation to evaporative exposure. The only noteworthy aspect of the results is the relatively high burning efficiencies obtained for the majority of the samples ignited (i.e. generally greater than 30%). As suggested by Hossain and Mackay, heavier oils may burn easier because the higher viscosity allows for intense local heating of the oil. Also, the heavier No. 4 oil samples exhibited sputtering during ignition presumably caused by local overheating of the oil or water in the samples. These "micro-explosions" may inject non-volatile oil into the flame resulting in better combustion.

In summary, there appears to be a clear dependence of flash and fire point on evaporative exposure with both parameters increasing as exposure increases. If the University of Toronto values are accepted as accurate, they further indicate that this dependence is more or less linear, with a substantial increase in flash and fire point with exposure for Prudhoe Bay crude and No. 4 fuel oil and a moderate increase with exposure for No. 2 heating oil. With regard to the effect of evaporative exposure on the overall burnability of the oil (i.e., ignition temperature, burn time, and burn efficiency), the combustion tests at the R&D Center provide only a sketchy picture at best. For the Prudhoe Bay crude, there appears to be some dependence as might be expected, since the crude oil contains a higher fraction of volatiles. However, the nature of this dependence is somewhat unclear as the results of the R&D Center analysis differ with those of previous researchers, who found an increase in burn time and burn efficiency with exposure up to a certain limiting value. For the No. 4 fuel oil there is no clear dependence of the combustibility parameters on evaporative exposure. Here the burnability appears to be less dependent on the fraction of volatiles, and more dependent on the variables affecting heat transfer (i.e., oil thickness, oil viscosity, and water content).

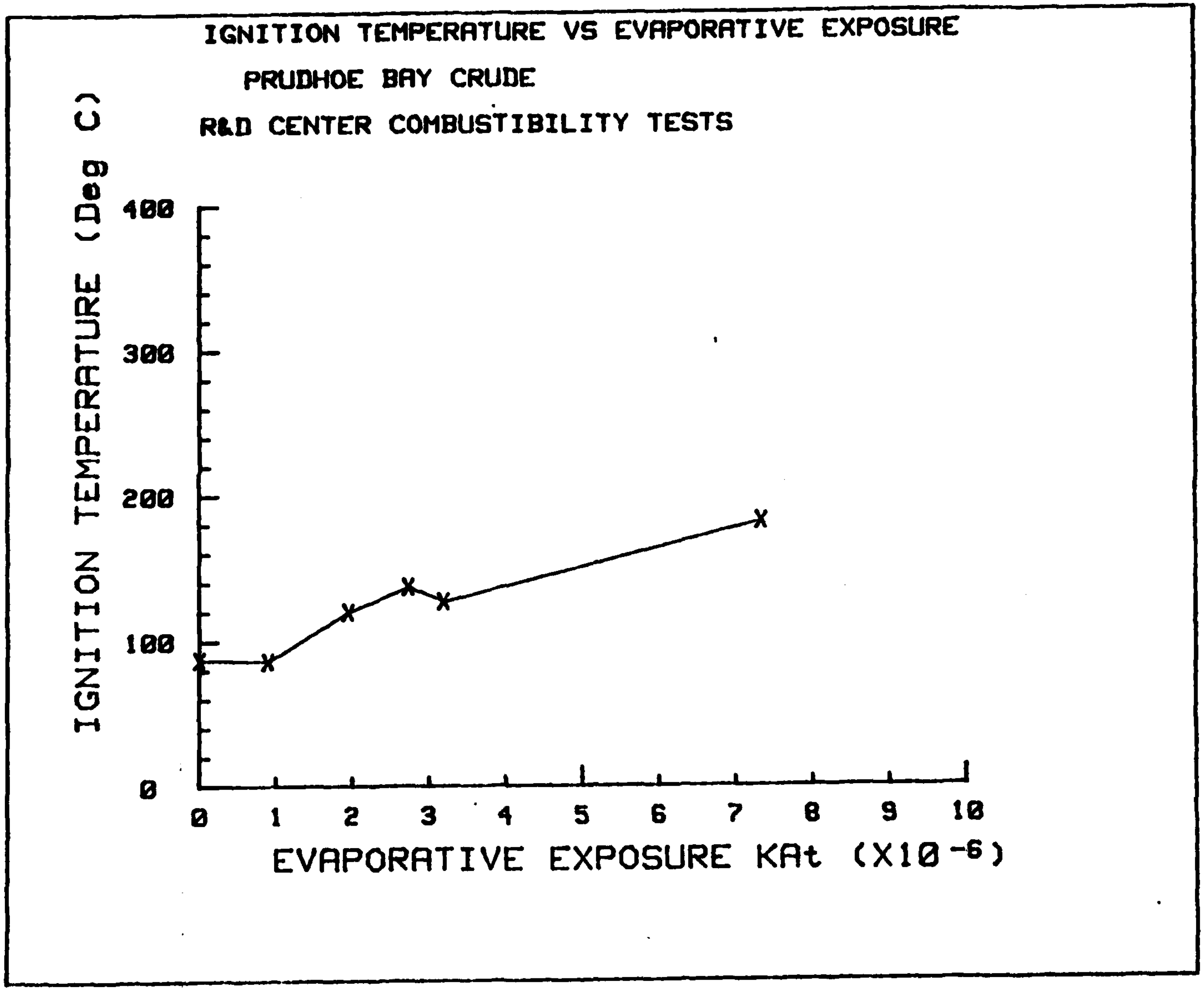

Figure 28a Ignition Temperature vs. Evaporative Exposure for Prudhoe Bay Crude Oil.

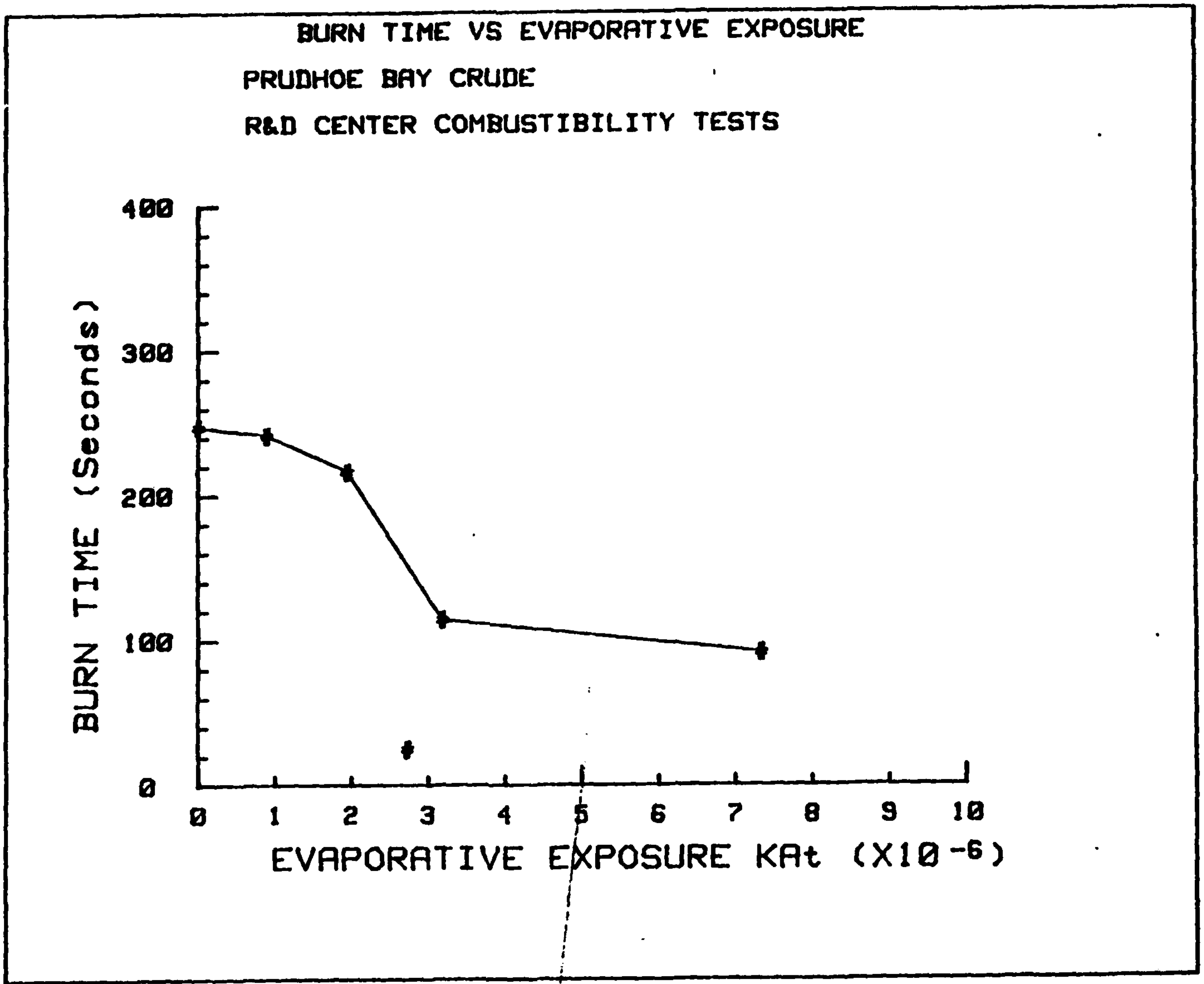

Figure 28b Burn Time vs. Evaporative Exposure for Prudhoe Bay Crude Oil.

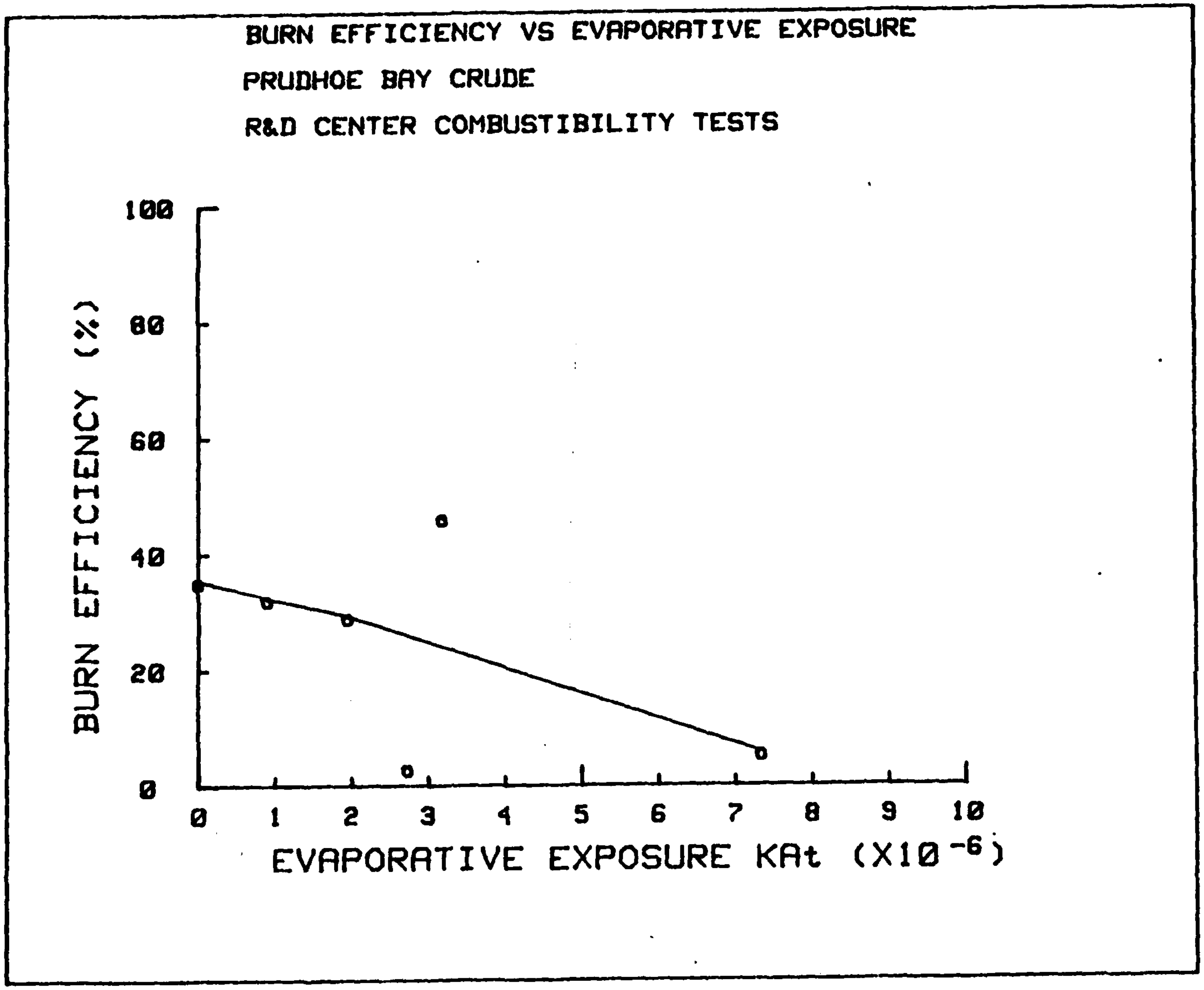

Figure 28c Burn Efficiency vs. Evaporative Exposure for Prudhoe Bay Crude Oil.

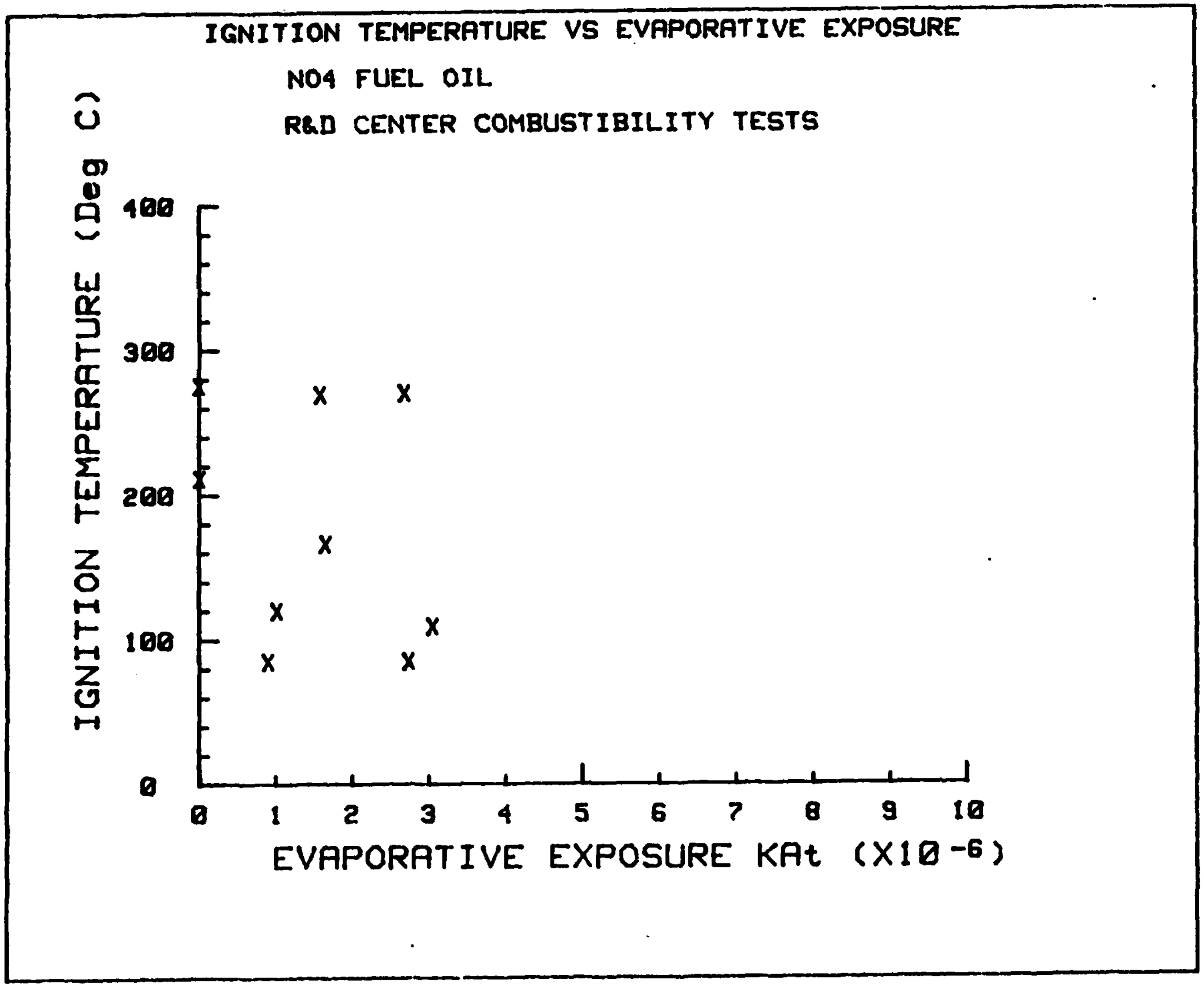

Figure 29a Ignition Temperature vs. Evaporative Exposure for No. 4 Fuel Oil.

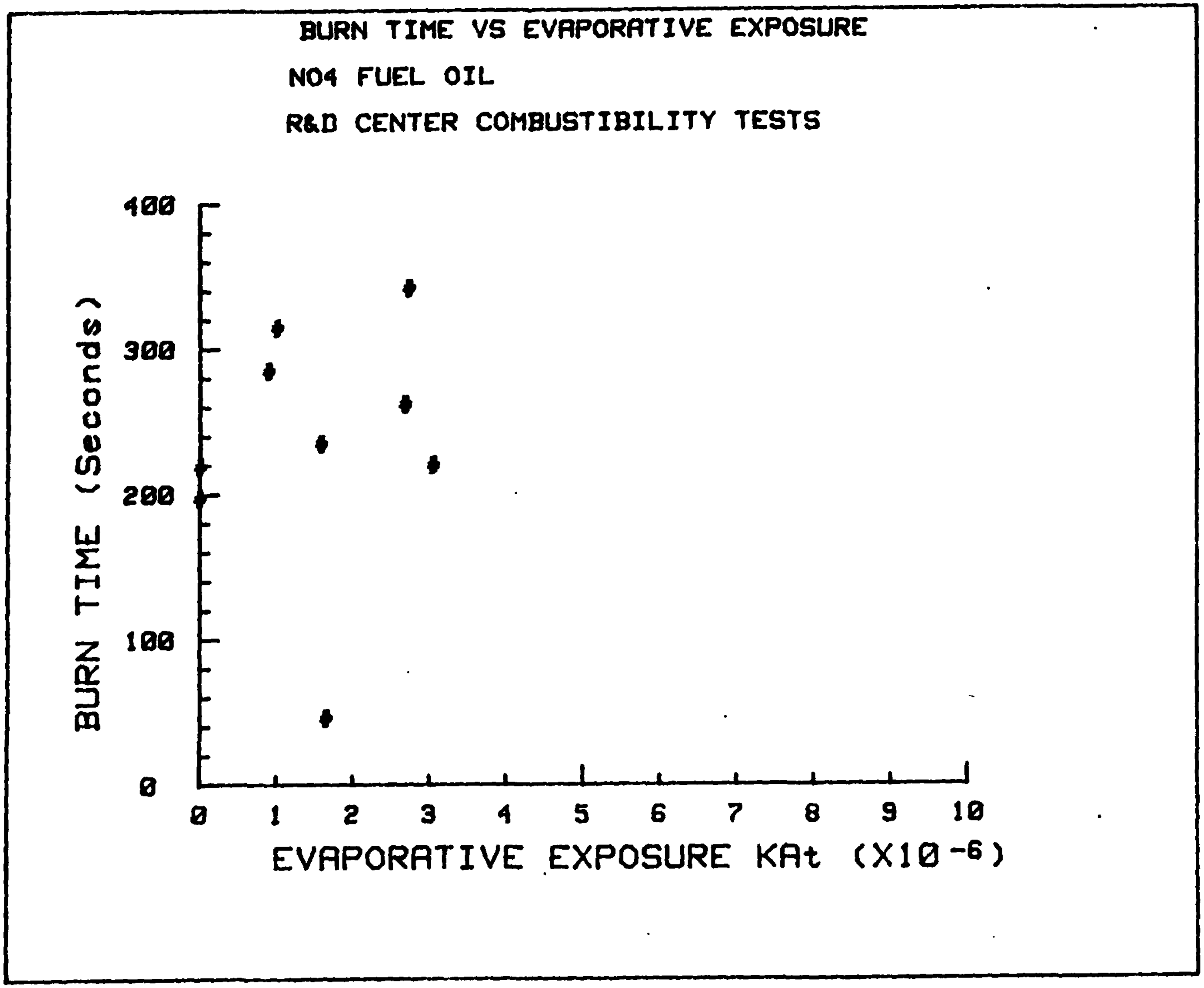

Figure 29b Burn Time vs. Evaporative Exposure for No. 4 Fuel Oil.

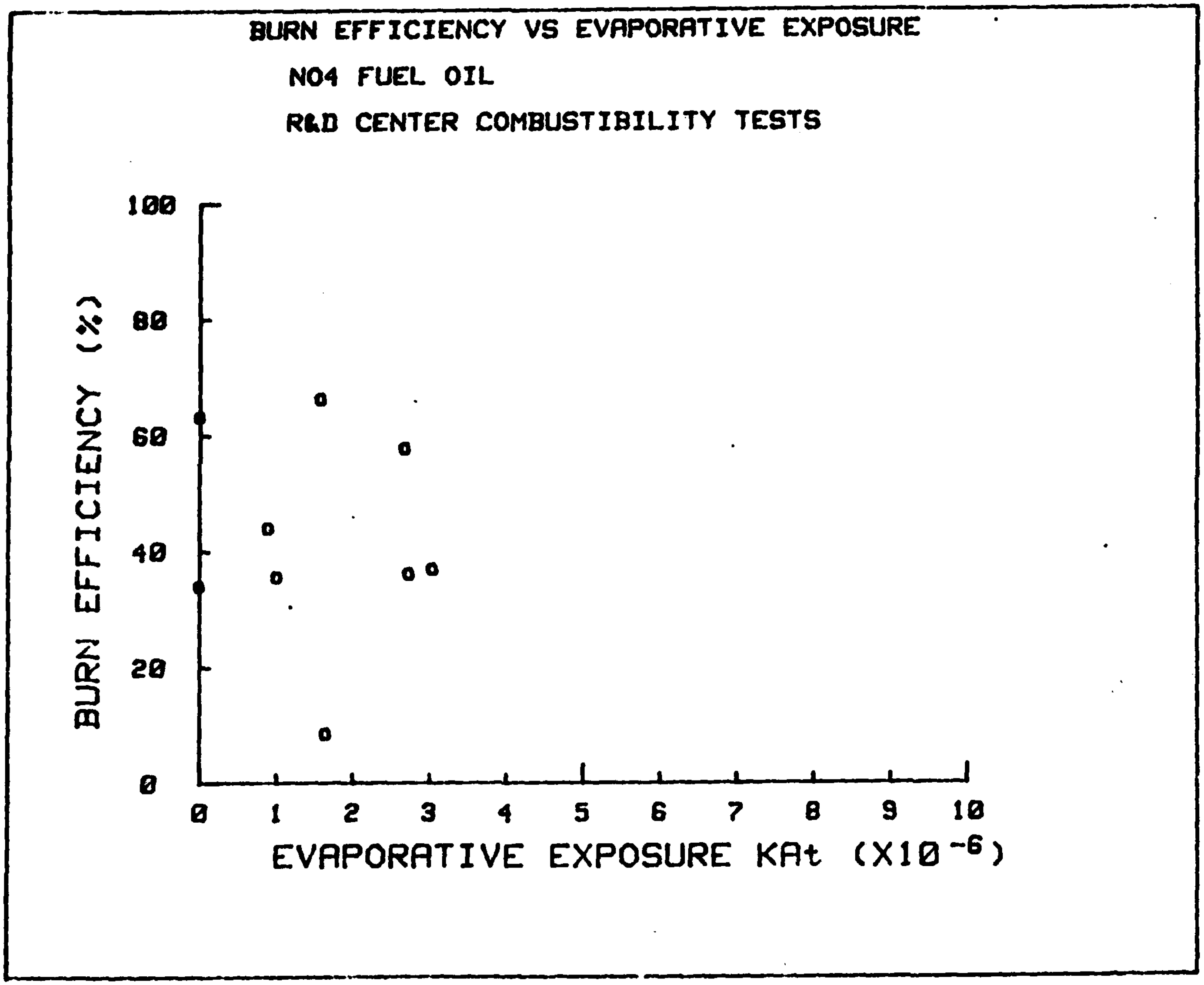

Figure 29c Burn Efficiency vs. Evaporative Exposure for No. 4 Fuel Oil.

6.5 Solar Radiation Analysis

As outlined in Section 2, the rate of evaporation of an oil spill is dependent on the oil vapor pressure at the air/oil interface, which is in turn dependent on the temperature at the air/oil interface. For thin oil slicks on open water, this is assumed to be equal to the underlying surface temperature. However, it is clear that for spills involving darker oils, and slicks of moderate thickness ($\approx$1cm) subject to intense solar radiation, the oil temperature may rise substantially above the underlying surface temperature. This temperature elevation effect may be particularly significant in the Arctic where the spilled oil is likely to be a darker crude oil, the oil spilled either on ice or in melt ponds where slicks will be thicker, and the underlying surface colder.

The implications of increased solar radiation absorption by oil and oiled ice on the depletion of Arctic pack ice have long been recognized (Campbell and Martin, 1973), and have been investigated in detail both theoretically and experimentally (Glaeser and Vance, 1971; Weir, 1975; NORCOR, 1975 and Walker, 1975). With regard to the effect of solar radiation on the weathering of oil, Nadeau and Mackay (1978) recognized the potential increase in evaporation rates due to the temperature elevation effect at the air/oil interface. In addition, experiments by Metge and Telford (1979) suggest that solar radiation may promote the formation of water-in-oil emulsions. However, to date very little work has been done to investigate the small-scale heat transfer mechanisms associated with oil temperature elevation, or quantify this phenomenon as a function of solar radiation levels and environmental conditions.

Accordingly, an exploratory study was conducted as part of the oil weathering experiment in which the solar radiation levels, air temperatures, underlying surface temperatures, and oil/air interface temperatures were continuously monitored for each type of oil during the Winter 1980/1981 season. Air temperatures were monitored using a YSI (Yellow Springs Instrument Co.) Series 400 air probe thermistor sheltered from direct solar radiation. Oil temperatures were monitored with YSI 400 surface probes which were positioned on the surface of the oil slick. Keeping the probe at the oil surface proved difficult during periods of rapid melting, precipitation, or high winds. However, with the darker oils, inspection of the data generally indicated whether the probe was properly positioned. Ice/water temperatures were monitored with a YSI 400 penetration probe positioned 5 centimeters below the ice/water surface.

Data analysis focused on the effect of solar radiation levels, air temperature, underlying surface type (solid ice, melt pool, open water), and underlying surface temperature on the air/oil interface temperature for two five-day periods in January and March 1981, respectively. These two periods were chosen as they hopefully simulate both spring conditions (solid ice or shallow melt pool with temperatures usually below freezing), and summer conditions (deeper melt pools or open water with temperatures above freezing) on the North Slope. Figures 30a through 30c show plots of oil surface temperature, underlying surface temperature, air temperature, and solar radiation levels (cal/cm^2 integrated over each hour) vs. time for three days within the study period. Figure 30a shows the situation where the oil is resting on a solid ice surface with air temperatures well below freezing. Here the

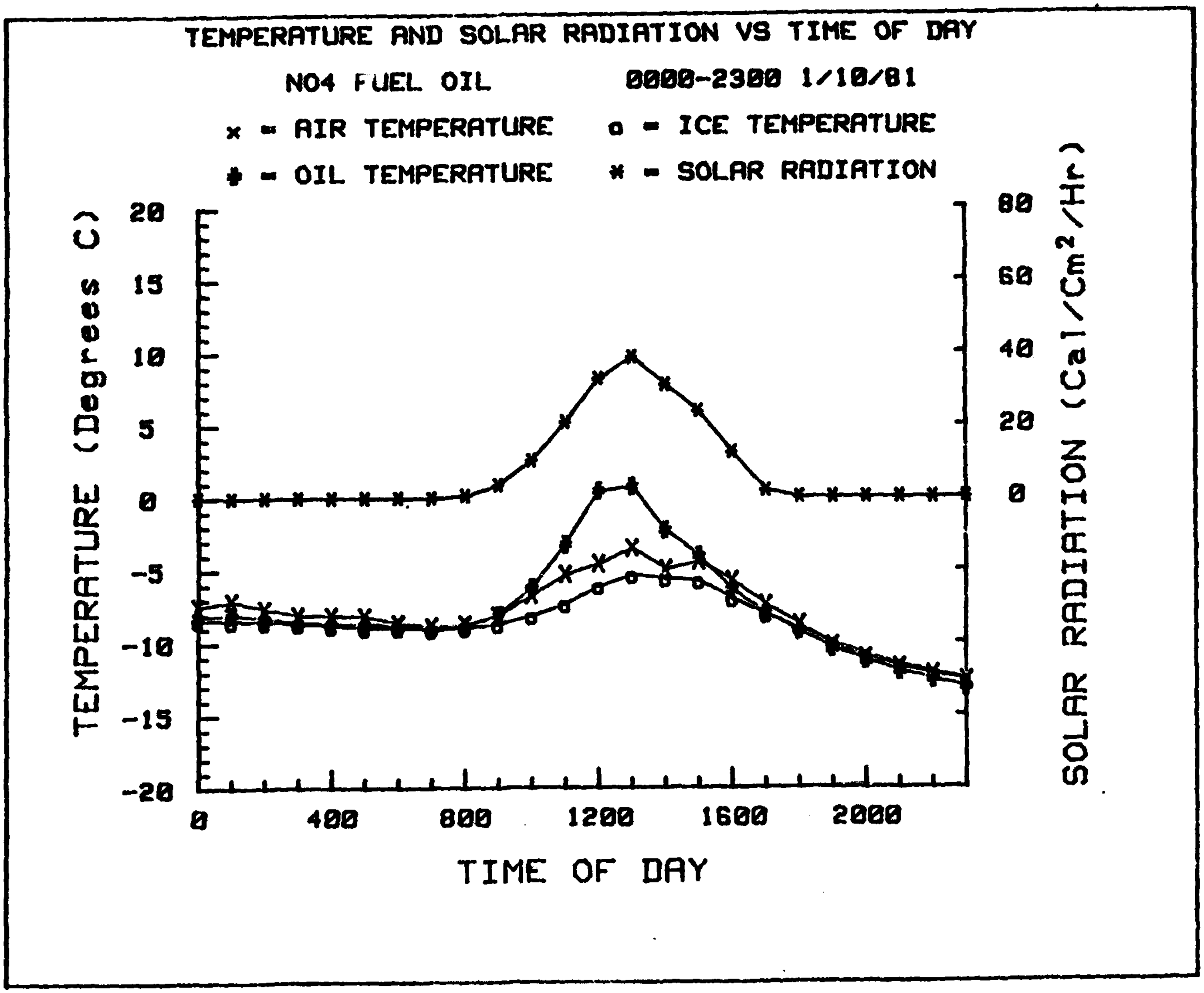

Figure 30a Air Temperature, Oil Temperature, Ice Temperature, and Solar Radiation vs. Time for 0000-2300, 10 January 1981.

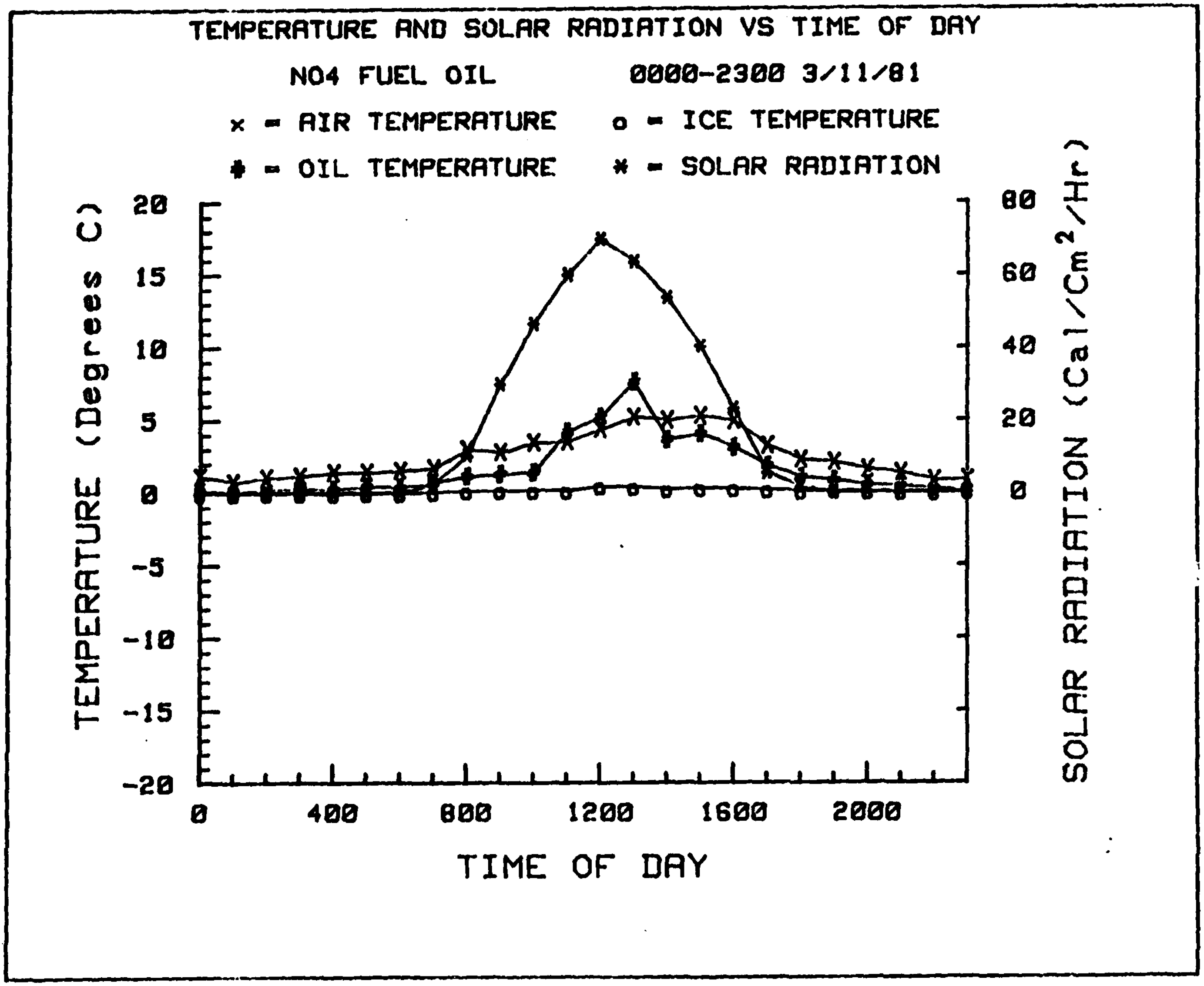

Figure 30b Air Temperature, Oil Temperature, Ice Temperature, and Solar Radiation vs. Time for 0000-2300, 11 March 1981.

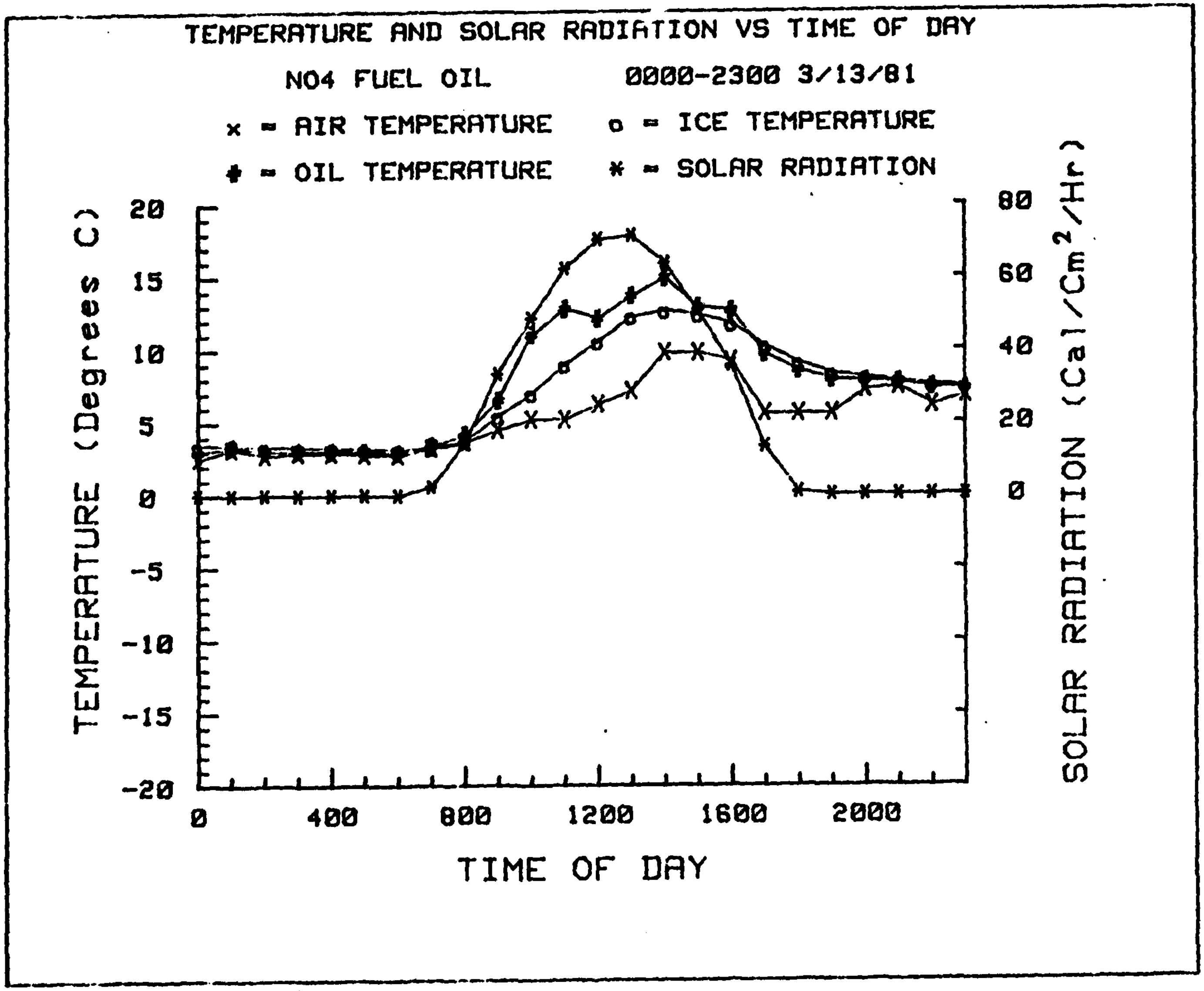

Figure 30c Air Temperature, Oil Temperature, Ice Temperature, and Solar Radiation vs. Time for 0000-2300, 13 March 1981.

effect of direct solar radiation on the oil temperature is quite evident with temperature elevations (oil temperature above surface temperature) up to 6.5°C. Figure 30b shows the situation where the oil is sitting on ice with a shallow melt pool forming during the day. Air tempertures are only a few degrees above freezing, but solar radiation levels are high as are the oil temperature elevation levels (up to 7.5°C). Figure 30c shows the situation where the oil rests in a deeper melt pool or open water. Air temperatures are well above freezing with high insolation values. Here oil temperatures are generally higher than in the previous two cases, but the oil is roughly the same temperature as the underlying water surface, presumably due to the more efficient transfer of heat from the oil to the water.

The results are presented in a different format in Figure 31 which shows oil temperature vs. underlying surface temperature. Data points where hourly integrated solar radiation values exceeded 20 cal/cm^2 are distinguished from data points where the hourly integrated solar radiation was less than 20 cal/cm^2. This figure shows that for lower solar radiation levels (less than 20 cal/cm^2 per hour), the oil temperature is generally equal to the underlying surface temperature. For higher insolation levels, temperature elevations of up to 10°C are possible. The figure further indicates that the highest temperature elevation values (10-11°C) are encountered in the shallow melt pool situation (underlying surface temperature -1°C to +1°C), suggesting a less efficient transfer of heat in this case. Temperature elevation levels on solid ice are also quite high, up to 6-8°C. In open water and deeper melt pools, the temperature elevations are less significant (3-4°C), so that the oil temperature can generally be approximated by the underlying surface temperature.

Having verified the general dependence of oil temperature elevation on solar radiation, the next step is to determine if any well-defined quantitative relation exists between these two parameters for a given underlying surface condition. Figures 32a through c give plots of oil temperature elevation vs. hourly integrated solar radiation values for solid ice, shallow melt pond, and deep melt pond/open water underlying surface conditions. In all three plots, the data appears to be more or less random with no well-defined functional relationship between oil temperature elevation and solar radiation levels.

It should also be noted that the oil spills in the weathering boxes were attempts to simulate spill and underlying surface conditions in the Arctic. The results are clearly subject to scaling errors, particularly for the deep melt pool/open water case, where the box of melt water does not represent an infinite heat sink, as does the open ocean. Hence the results outlined above should be treated as qualitative in nature.

In summary, it is clear that direct solar radiation will raise the temperature of a darker oil, spilled on the ice. However, there appears to be no simple quantitative dependence of the oil temperature on the intensity of the solar radiation alone. The oil temperature elevation is more likely a complicated function of all parameters affecting the heating of the oil and the heat flux to the underlying surface (e.g., solar radiation, air temperature, oil thickness, oil viscosity, water depth, wind speed, etc.) making the formulation of a simple quantitive model difficult based on the limited data of this experiment.

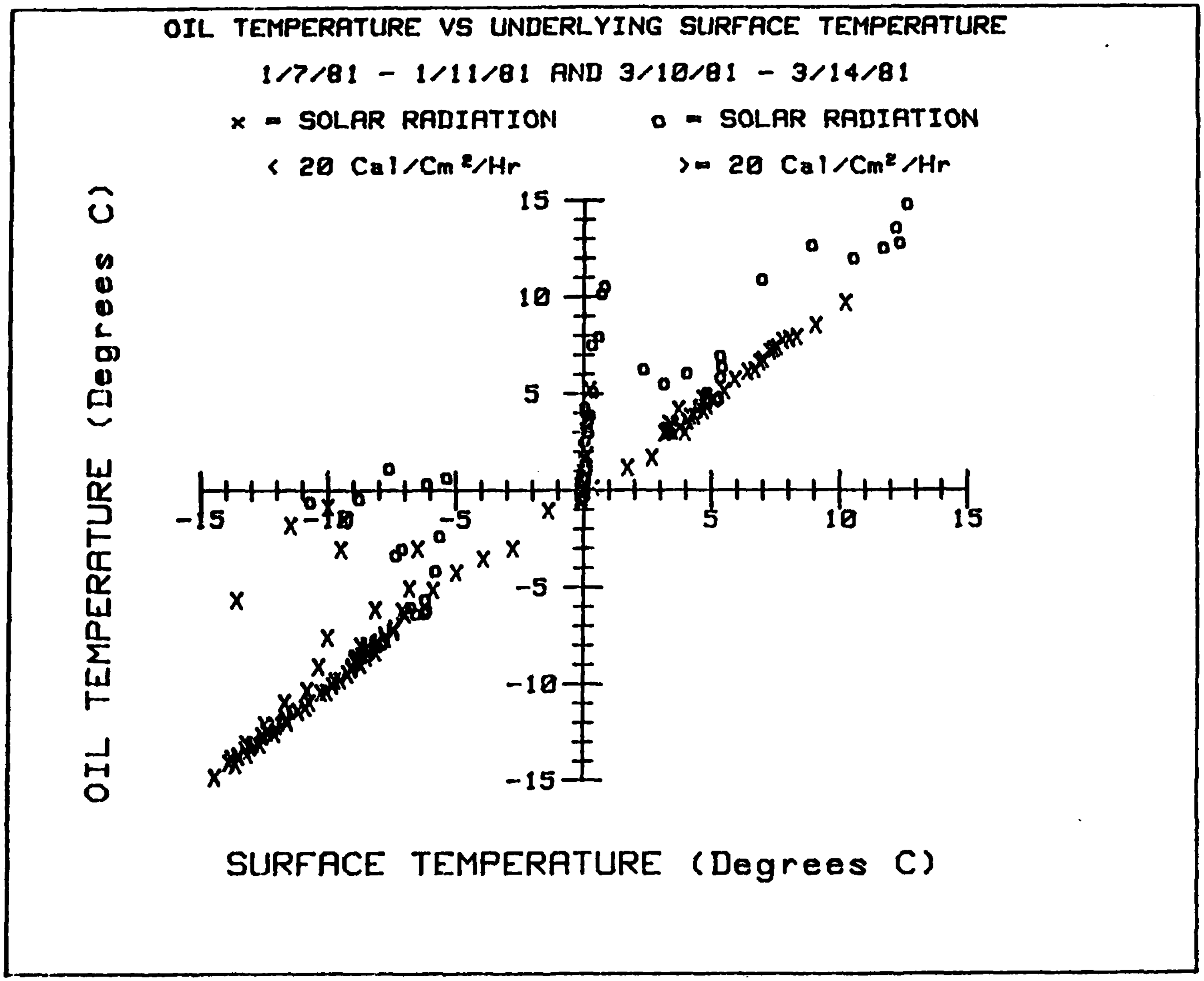

Figure 31 Oil Temperature vs. Ice Temperature for Periods 7 Jan - 11 Jan 1981 and 10 March - 14 March 1981.

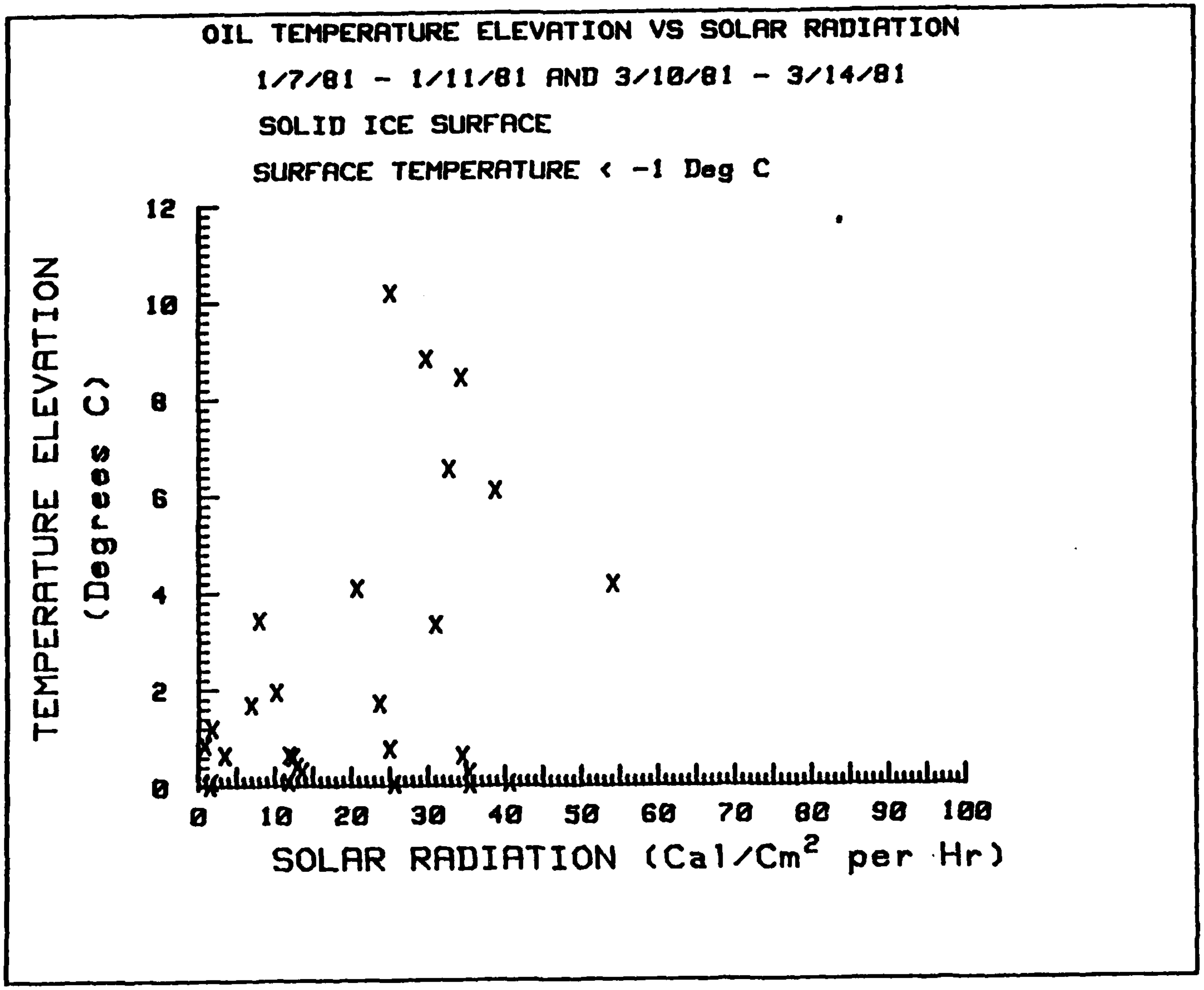

Figure 32a Oil Temperature Elevation vs. Hourly Integrated Solar Radiation for Oil on Solid Ice (Underlying Surface Temp < -1^{o} C).

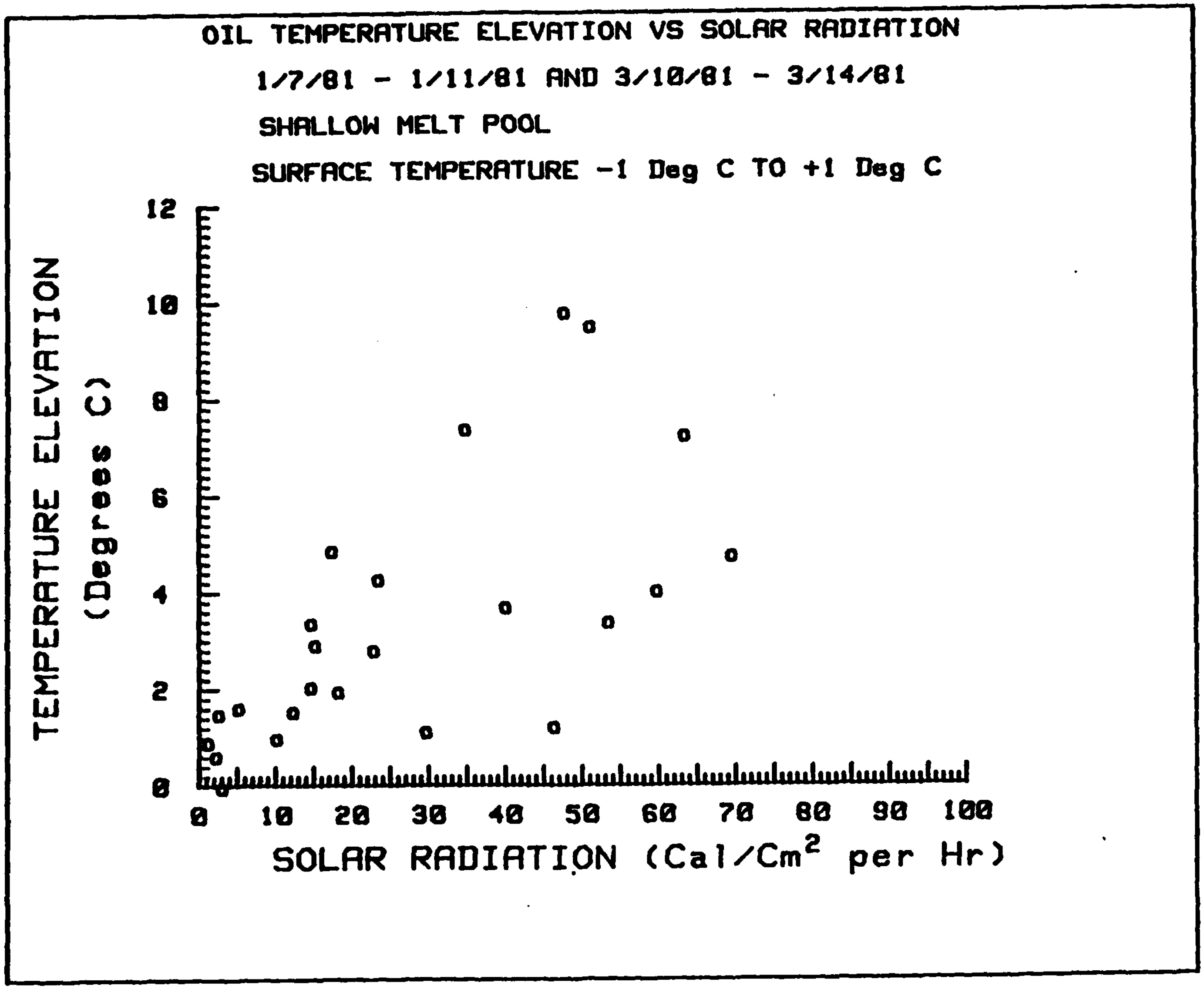

Figure 32b Oil Temperature Elevation vs. Hourly Integrated Solar Radiation for Oil in a Shallow Melt Pool (Underlying Surface Temp -1°C to +1°C).

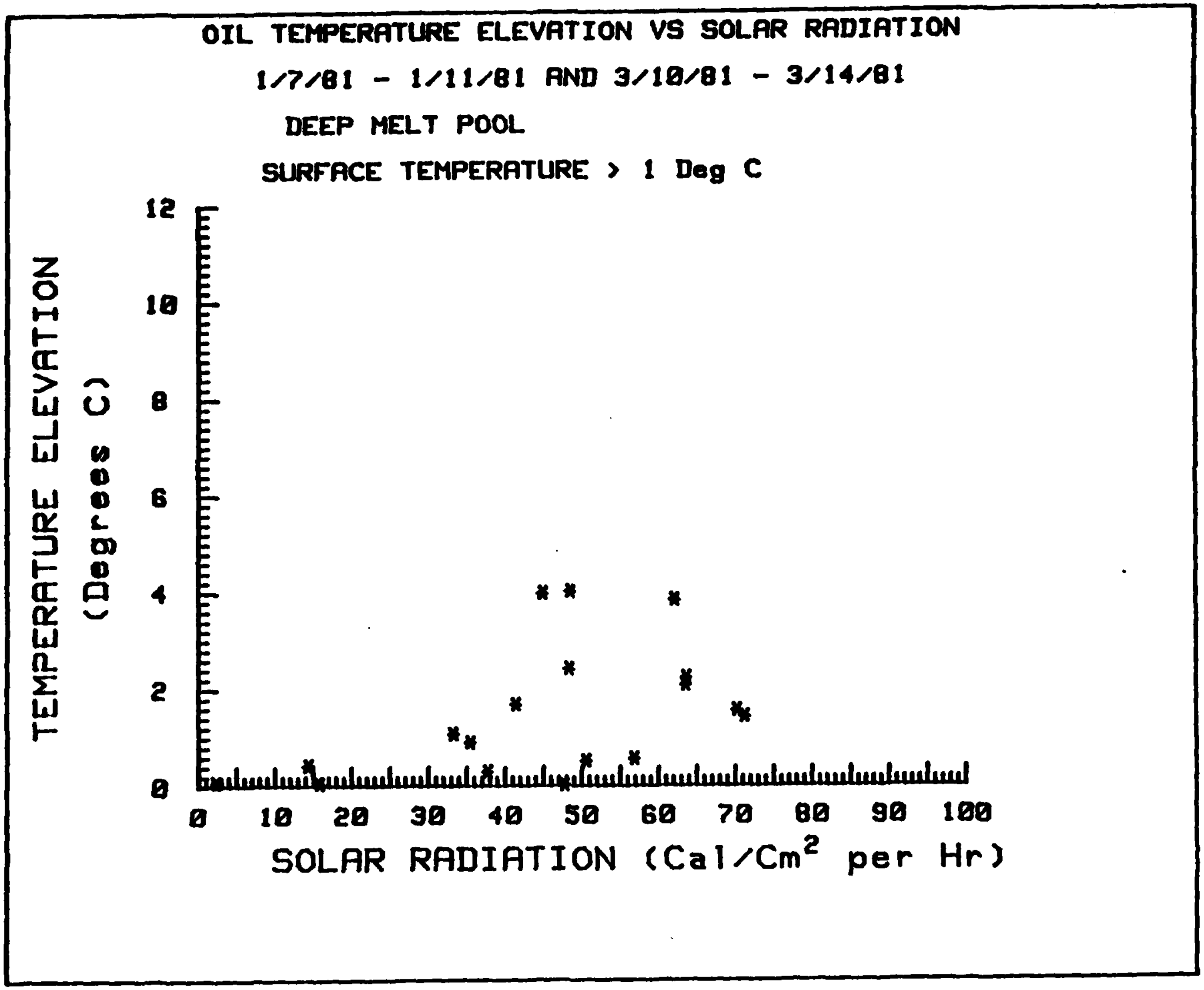

Figure 32c Oil Temperature Elevation vs. Hourly Integrated Solar Radiation for Oil in Deep Melt Pool/Open Water (Underlying Surface Temp> $+1^{o}C$).

In terms of predicting the evaporation rates of oil, this temperature elevation effect may be merely a point of scientific interest. The evaporation curves of Nadeau and Mackay (Figure 2) indicate that even a 10°C error in estimating the oil/air interface temperature will only result in slight errors in predicting the mass fraction remaining. Therefore, the air/oil interface temperature can probably be approximated by the underlying surface temperature. The effects of direct solar radiation and oil temperature elevation on the chemical composition of the oil, and the degree of emulsification may be more significant.

7.0 CONCLUSIONS

It should be stressed that the R&D Center weathering experiment was an attempt to simulate an oil spill in the Arctic during late spring and summer. The results presented above are therefore subject to scaling errors, and errors associated with the difference in environmental conditions in the Arctic and at the test site. Extrapolation of the results to actual spill conditions in the Arctic should be done with considerable caution. It is in recognition of the exploratory nature of the experiment that the following conclusions are presented.

1. The mass fraction remaining vs. evaporative environmental exposure data are inconclusive due to inaccuracies in the sample analysis procedures.

2. The density vs. evaporative exposure plots show a well-defined increase in density with evaporative exposure except where the oil samples were emulsified. Emulsification can increase oil density significantly, independent of evaporative exposure levels. This increase in density is particularly important for the heavier oils whose density may approach that of sea water, in that it may determine the vertical location of the oil in the ice. For oils where emulsification is not a factor, the increase in density can probably be modeled as a function of evaporative exposure.

3. The oil/water interfacial tension vs. evaporative exposure plots show that interfacial tension decreases with weathering for all three oils; however, there is no well-defined quantitative relation between interfacial tension and evaporative exposure. This decrease of interfacial tension with weathering may have important implications on the horizontal and vertical spread of an oil spill in an ice-infested environment.

4. The aqueous solubility of all three oils decreased rapidly with weathering. There also seems to be a clear functional relationship between solubility and evaporative exposure. This decrease in oil solubility has important implications on the toxicity of the oil to marine life, particularly for the Prudhoe Bay crude. In certain cases, it may be advisable to let the oil weather on ice for a period of time before allowing it to enter the water.

5. The viscosity vs. evaporative exposure plots show that viscosity increases with evaporation for the Prudhoe Bay crude and No. 4 fuel oil, with little change in viscosity for the No. 2 heating oil. The results also show that the viscosity of the heavier oils is highly sensitive to emulsification, with emulsified samples attaining viscosity values of 10,000 cp independent of evaporative exposure levels. This sensitivity may complicate the modeling of viscosity as a function of evaporative exposure. These higher viscosity values will have important implications on the cleanup of the spill, making many of the conventional cleanup techniques ineffective.

6. The pour point vs. evaporative exposure plots show a well-defined increase in pour point as a function of evaporative exposure. Likewise, the pour point appears to be relatively insensitive to emulsification. This increase in pour point has some significance with regard to cleanup strategy in that some cleanup methods (use of suction hoses, skimmers, etc.) will obviously be ineffective if the oil temperature is below the pour point. Perhaps more important are the implications on the accuracy of fluid dynamic

models for oil movement and behavior when the oil is near the pour point (i.e., ceases to behave like a fluid).

7. The gas chromatograph analysis shows a well-defined relationship between the C_{12}/C_{20} and C_{14}/C_{20} ratios and evaporative exposure for samples within a given sample group. However, the C_{12}/C_{20} ratios also delineate differences in chemical composition between sample groups, independent of the levels of evaporative exposure. Hence, the C_{12}/C_{20} and C_{14}/C_{20} ratios may be a valuable weathering index as suggested by Flanigan and Bentz (1977), particularly if correlated directly with the changes in the physical properties and combustibilities of the various oils.

8. The plots of flash and fire point show a clear dependence on evaporative exposure with both parameters increasing as exposure increases. If the University of Toronto values are accepted as accurate, the dependence is more or less linear, with a substantial increase in flash and fire point for Prudhoe Bay crude and No. 4 fuel oil, and a moderate increase for No. 2 heating oil.

9. With regard to the effect of evaporative exposure on overall burnability, the results of the R&D Center oil/ice combustibility tests are quantitatively inconclusive, and in conflict with the results of previous researchers. In a qualitative sense, the results indicate that No. 2 heating oil will be difficult to ignite if spilled on ice. On the other hand, Prudhoe Bay crude and No. 4 fuel oil generally ignited at evaporative exposure values less than 7×10^6, and may burn with reasonable efficiency on ice (30-50% for Prudhoe Bay crude and 30-70% for No. 4 fuel oil).

10. Results of the solar radiation analysis indicate that direct solar radiation will raise the temperature of a darker oil spilled on ice. However, there appears to be no simple quantitative dependence of the oil temperature on the intensity of solar radiation alone. The oil temperature is more likely a complicated function of all parameters affecting the heating of the oil, and the heat flux to the underlying surface. In terms of predicting the evaporation rates of an oil spill, this oil temperature elevation may be merely a point of scientific interest as the analysis indicates maximum temperature elevations of about 10°C. This increase in temperature during a few hours of the day will have little effect on the overall evaporation rate.

8.0 SUGGESTIONS FOR FURTHER RESEARCH

In view of the results of this exploratory effort, it is clear that several key areas warrant further research.

1. There is a well-defined quantitative relationship between the various physical properties and evaporative exposure levels, particularly in cases where emulsification has not occurred. Hence, the development of an operational physical properties model based on evaporative exposure estimates should be investigated. Such a study is presently being undertaken by the University of Toronto under contract with the Coast Guard R&D Center.

2. The results also indicate that several physical properties of the oil, and the combustibility of the oil, are sensitive to the degree of emulsification. However, there are essentially no quantitative data on the emulsification of oil under Arctic conditions. Therefore a study should be undertaken to determine the susceptibility of various types of oil to emulsification as a function of environmental conditions and the degree of turbulent mixing. The physical properties of the oil, particularly Prudhoe Bay crude, should also be cataloged as a function of the degree of emulsification. Such a study might include an exploratory weathering experiment similar to the one described above in which the oil would be weathered in pans on the ice, but with the oil isolated from the water surface. One set of samples would be exposed to direct solar radiation, while another set would be shaded. The samples would be weathered for periods of up to a month. Portions of each sample would then be subject to a known amount of mechanical mixing with water at $0^{o}C$, and the degree of emulsification of the oil (water content) measured. The physical properties of each emulsion would also be measured. This would allow cataloging of the susceptibility to emulsification as a function of environmental conditions (evaporative exposure, solar radiation, etc.), and the physical properties of the emulsion as a function of the degree of emulsification.

3. The combustibility data from the weathering experiment is cursory in nature and largely inconclusive. As in-situ burning may be the only feasible countermeasure to an open ocean spill in the Arctic, it is clear that additional research is warranted. Additional research should include both laboratory and field experiments in which the combustibility of the oil is quantitatively documented (i.e., ignition temperature, burn time, and burn efficiency measured) as a function of evaporative exposure and degree of emulsification. In addition, the effect of oil/ice configuration (i.e., oil on solid ice, oil in shallow melt pool, oil trapped in a lead, oil in broken ice, etc.) and the effect of oil slick thickness should be investigated.

4. The results of the gas chromatograph analysis indicate that the C_{12} and C_{14} peaks may provide a weathering index which could be utilized in an actual spill situation when the duration of the weathering period (i.e., evaporative exposure) is unknown. Additional research should focus on correlating the physical properties and combustibility of the weathered oil directly with the C_{12}/C_{20} and C_{14}/C_{20} ratios, as these ratios may provide a better estimate of the degree of weathering than the evaporative exposure estimates. If a well-defined correlation exists between these ratios and the physical properties and combustibility of the oil, then a real-time GC analysis of the spilled oil could provide the on-scene coordinator with

important information on the physical state of the spill. Such GC analyses are often conducted as a routine procedure to determine the source of the spill.

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APPENDIX A
SPECIFICATIONS FOR ENVIRONMENTAL MONITORING INSTRUMENTATION

Instrument: Instrulab 2000 Datalogger with YSI Series 400 Thermistors

Parameters Monitored: Air temperature, oil temperature, ice/water temperature

Manufacturer: Datalogger - Instrulab, Inc.
1205 Lamar Street
P.O. Box 426
North Dayton Station
Dayton, Ohio 45404

Thermistors - Yellow Springs Instrument Company, Inc.
Yellow Springs, Ohio 45387

Data Specifications:

Range $-30^{o}C$ to $+85^{o}C$
Accuracy $\pm 0.10^{o}C$ (-30^{o} to $+10^{o}C$)
$\mp 0.30^{o}C$ ($-30^{o}C$ to $+85^{o}C$)
Resolution $\overline{0}.01^{o}C$

Instrument: MRI Mechanical Weather Station

Parameters Monitored: Wind Speed and Air Temperature

Manufacturer: Meteorology Research, Inc.
Box 637
464 West Woodbury Road
Altadena, California 91001

Data Specifications: Wind Run (Speed)

Range up to 60 mph
Threshold 0.75 mph
Accuracy 0.5 mph or 2% full scale

Temperature

Range $-30^{o}F$ to $+120^{o}F$
Accuracy $+ 3^{o}F$
Resolution $\overline{1}^{o}F$

Instrument: Eppley PSP Pyranometer

Parameter Measured: Solar Radiation

Manufacturer: The Eppley Laboratory, Inc.
12 Sheffield Avenue
Newport, RI 02840

Data Specifications: Pyranometer

-Conversion 6.45 mV/cal cm^{-2} min^{-1}
-Linearity with temperature + 1%, -20 to +40°C
-Linearity with intensity $\pm$ 0.5% for 0 to 4.015 x 10^8 cal cm^{-2} min^{-1}
-Sensitivity 9 mV per 8.60 x 10^6 cal cm^{-2} min^{-1}

Integrator

-Accuracy 1.0 cal/cm^2
-Resolution 0.1 cal/cm^2

Instrument: Hollis MR-5 Pyranometer with Instrulab 2000 Datalogger Recording

Parameter Measured: Instantaneous Solar Radiation

Manufacturer: Pyranometer - Hollis Observatory
One Pine Street
Nashua, NH 03060

Data Specifications: Pyranometer

-Conversion 49.33 MV per cal cm^{-2} min^{-1}
-Linearity with temperature + 1.5% -20 to +40°C
-Linearity with intensity $\pm$ 1% up to 2 cal cm^{-2} min^{-1}

Datalogger

-Range 0 to + 275 mV
-Accuracy $\pm$ 0.025% of Reading
-Resolution 10 V

APPENDIX B
OIL SAMPLE ANALYSIS CONDUCTED
AT THE COAST GUARD R&D CENTER

Mass Fraction Remaining

The mass fraction remaining for each No. 2 heating oil, No. 4 fuel oil, and Prudhoe Bay crude oil sample was determined by measuring the initial oil volume (i.e., 400 ml), and comparing this with the final oil volume recovered from the ice block at the end of the weathering period. Oil, oily water, and oiled ice were recovered from the weathering boxes to the extent physically possible under the varying conditions, and placed in a separatory funnel. The samples were then kept in the funnel at room temperature until the oil separated out. Final volumes were read from the scale on the separatory funnels to the nearest 5 ml. The mass fraction remaining values were subject to substantial errors due to oil blowing and splashing from the boxes, sticking to the implements used to recover the oil, and the inclusion of water in the oil due to emulsification. Because of their nature, these errors were all but impossible to quantify. Mass fraction remaining values were also obtained for the No. 6 fuel oil (Samples 7-13) with initial and final mass determined by weight instead of by volume, due to the semi-solid nature of the oil.

Specific Gravity (Density) at 25°C

Initial values of specific gravity (density) were obtained following the general procedures outlined in ASTM Method D 369-67 for the No. 2 heating oil, No. 4 fuel oil, and Prudhoe Bay crude; and ASTM Method D 70-76 for No. 6 fuel oil. The reference temperature for both methods was specified as 25°C. Gay-Lusac type pycnometers (10 ml) were used for the No. 2 heating oil, while Hubbard type pycnometers (25 ml) were used for the Prudhoe Bay crude, No. 4 fuel oil, and No. 6 fuel oil. Specific gravities were converted to densities using the conversion density = specific gravity x 0.99707, where 0.99707 is the density in gm/cm^3 distilled water at 25°C.

Viscosity at 20°C

Initial values of viscosity were obtained using a Brookfield model LVF viscometer. Stated accuracy for this instrument is 1% of full scale, so that the maximum accuracy is 1 centipoise. Measurements were made in a 300 ml tall form beaker, so that approximately 200 ml of sample were required to give reasonable results. For this reason, it was not possible to obtain values for all the samples. Sample temperature was maintained at $20^\circ C \pm 1^\circ C$ in a water bath. Three measurements were taken on each sample and the mean recorded as the actual value. When a particular reading showed wide variation from the other two, the value was rejected and a substitute reading obtained. Viscosity measurements obtained by this method were treated as approximate values, and were used primarily to select samples for more accurate viscosity determination by the University of Toronto.

Water Content (Emulsification)

Because some of the samples had obviously become emulsified during the weathering period, each sample was analyzed in a cursory manner to determine water content. This was accomplished by placing 2 ml of oil and 10 ml of pentane in a centrifuge tube, and centrifuging for 5 minutes. During this process, any appreciable amount of water in the sample would accumulate at the bottom of the tube. The amount of water was read to the nearest 0.1 ml using the scale on the centrifuge tube. This value was then used to compute the % oil vs. water in the sample. The water content analysis was done, not so much to quantify the degree of emulsification, but rather to clearly identify those samples that had become emulsified.

Gas Chromatograph Analysis

Gas chromatograph scans for the weathered samples were run on a Perkin-Elmer Model 3920 Gas Chromatograph with a 50-inch SCOT (support coated open tubular) OV 101 column (#SC203) at air pressure of 50 lb-in^2. A Flame Ionization Detector (FID) was used reading on the 800 scale. Sample size was 0.2 1. The No. 2 heating oil and No. 4 fuel oil samples were run without processing, as were Prudhoe Bay crude samples 9 through 35. Prudhoe Bay crude samples 1 through 8 were deasphalted using the standard DDC technique. All gas chromatograph analyses were conducted under the direction of Dr. George M. Frame of the R&D Center Chemistry Branch. Data analysis included measuring the heights of the various GC peaks on the graphic output trace (C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, C_{20}), and computing the ratios of each peak to the C_{20} peak (i.e., C_{10}/C_{20}, C_{12}/C_{20}, C_{14}/C_{20}, C_{16}/C_{20}, C_{18}/C_{20}).

Flash Point and Fire Point

Flash point and fire point values for the weathered oil samples were obtained with a precision Cleveland open cup flash tester following the procedure outlined in ASTM D-92. Values were read from the thermometer to the nearest 1°C. Flash and fire point testing was limited by the sample volume in that 75 ml of the sample were needed for the test, and this portion of the sample could not be used for other tests. In addition, it proved impossible to obtain values for emulsified No. 4 fuel oil and Prudhoe Bay crude samples as vaporization of water in the oil caused the sample to boil out of the test cup prior to reaching the flash point, making the procedure both inaccurate and dangerous. For these reasons, only a portion of the total number of samples was tested.

Combustibility

Because the R&D Center weathering studies focus on the implications of weathering on oil spill countermeasures, a simple laboratory burning test was devised to quantify the combustibility of the weathered oil under Arctic conditions. The tests were conducted indoors under a laboratory ventilation hood (see Figure 21a), as preliminary tests outdoors resulted in the wind prematurely extinguishing the flame. The procedure called for placing a measured sample (50 ml for No. 2 heating oil and 100 ml for Prudhoe Bay crude) into an aluminum foil pan 20 cm in diameter. These volumes were chosen in that they represent a reasonable oil spill thickness as might be found for oil on ice (i.e., 0.16 cm for No. 2, 0.32 cm for No. 4 and Prudhoe Bay crude).

Each oil sample was weighed to the nearest 0.1 gram. The pan was placed on a large block of ice in a large metal tray, and the oil allowed to cool. Ambient air temperature and initial oil temperature were measured using an Omega 5800-2 thermistor thermometer with YSI Series 700 thermistors (accuracy $\pm$ 0.5°C, resolution $\pm$ 0.1°C). Air temperatures were typically 20-25°C. Initial oil temperatures were 0-5°C.

The oil was then heated at the center of the pan using a propane torch until continuous burning (ignition) was attained. The temperature at the surface of the oil in the center of the pan was continuously monitored using an Omega Model 870 Digital Thermometer with a Type K Thermocouple probe (resolution 1°C, accuracy $\pm$ 0.25% of reading $\pm$ 1°C). Parameters monitored throughout the burn included:

Ignition time: The time in seconds between the application of the torch and ignition of the oil.

Ignition temperature: The temperature (°C) at which ignition occurred, i.e., when continuous burning could be sustained after removal of the torch flame.

Burn time: The time in seconds between the ignition of the oil and final burnout.

Maximum burn temperature: The maximum temperature attained as the oil burned.

Once the flame went out, the oil was allowed to cool and then reweighed to the nearest gram. The burning efficiency was then calculated as:

$$\text{Burn Efficiency \%} = \frac{\text{mass of oil burned}}{\text{initial oil mass}} \times 100$$

Two major problems were encountered which prevented the obtaining of combustibility data for all the samples. The first was the availability of a sufficient volume of sample after all the other tests had been run. The second was the presence of water in the sample (emulsification) which prevented ignition in many of the No. 4 and Prudhoe Bay crude samples.